



**US Army Corps  
of Engineers®**  
Engineer Research and  
Development Center

*Strategic Environmental Research and Development Program*

## **Characterization and Fate of Gun and Rocket Propellant Residues on Testing and Training Ranges: Interim Report 1**

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**Abstract:** The objectives of the research described in this report are to characterize the deposition and accumulation of propellant residues at the various types of firing points at military firing ranges, develop process descriptors to allow estimation of environmental transport rates of individual energetic chemicals from these residues, and collect lysimeter and groundwater monitoring well samples to experimentally assess off-site transport of residues. Estimates of residue deposition are presented for the firing of 60- and 81-mm mortars and 105-mm howitzers. Experimental results are provided for propellant residue accumulation at antitank rocket, mortar, artillery, and small arms ranges at several installations. Results from soil column experiments on the transport of nitroglycerin, nitroguanidine, and diphenylamine also are presented with resulting transport property estimates. Also, an experiment to assess the deposition of ammonium perchlorate from Mk58 rocket motors is described.

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## Preface

This report was prepared by the U.S. Army Engineer Research and Development Center (ERDC), Cold Regions Research and Engineering Laboratory (CRREL), Hanover, New Hampshire, and Environmental Laboratory (EL), Vicksburg, Mississippi, in partnership with Defence Research and Development Canada - Valcartier (DRDC-Val), Quebec. The research was sponsored by the Strategic Environmental Research and Development Program (SERDP), Arlington, Virginia, Bradley P. Smith, Executive Director, and Dr. Jeff Marqusee, Technical Director, under Environmental Restoration Project Number ER-1481. The principal investigator was Dr. Thomas F. Jenkins, Environmental Sciences Branch (ESB), CRREL. Co-principal investigators were Dr. Judith C. Pennington, Environmental Processes and Engineering Division (EPED), EL, and Dr. Guy Ampleman, DRDC-Val.

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# **1      Introduction**

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## **Background**

Live-fire training is a necessary component of readiness for the armed forces of the United States and Canada. To sustain the long-term use of Department of Defense (DoD) training ranges, each installation must comply with environmental regulations ensuring that human health and the environment are not unacceptably compromised. In particular, the DoD must ensure compounds produced by live-fire training residues do not migrate beyond installation boundaries at concentrations that impair the use of ground and surface water resources for the surrounding communities. Currently, the liability posed by off-site migration of propellant residues at military training ranges is unknown. Little or no environmental data exist on residues from newer composite formulations and uncertainty remains in the understanding of the fate of some energetic compounds and stabilizers in more conventional nitrocellulose- (NC) base propellants. Assessing the deposition, accumulation, and fate of residues associated with propellants at training range firing points will further the Army's goal of quantifying potential contaminants of concern.

### *Gun and small rocket propellant formulations*

#### **Composition**

Solid propellants for guns, artillery, and mortars are low-explosive materials designed to burn at a controlled rate and rapidly produce gases that create the pressure to accelerate projectiles from guns or propel rockets toward targets (U.S. Army 1990, Folly and Mäder 2004). The rapid but controlled burning of low explosives such as propellants is known as deflagration. Formulations contain several components, with the primary being an energetic material, commonly a nitro-containing organic chemical such as NC. Also included are compounds that modify burn rate, binders or plasticizers (both energetic and inert) that enable loading and packing the propellant into the shell, and lastly, compounds that absorb nitrogen oxides, the breakdown products of NC, to increase propellant stability during storage. Solid propellants used for rocket fuel (termed "composite") include an oxidizing solid (such as powdered aluminum or barium nitrate) together with an organic binder, which acts as a fuel.

Solid propellants with NC are divided into three classes based on presence of added energetic compounds (Table 1-1). Single-base propellants contain NC alone as the principal energetic material. Double-base propellants contain NC infused with a liquid organic nitrate, such as nitroglycerin (NG), which can gelatinize the NC. Triple-base propellants include the two double-base compounds NC and NG along with nitroguanidine (NQ), also known as picrite. NQ has an explosive power similar to that of NG, but burns at a lower temperature, thereby reducing erosion in the gun barrel and reducing flash.

<b>Table 1-1. Summary of solid propellant classes with common examples.</b>			
Type	Examples	Particle type <sup>1</sup>	Principal ingredients
Single base	M1	Single- or multi-perforated cylinder	NC, 2,4-DNT
	M6	Multi-perforated cylinder	NC, 2,4-DNT
	M10	Flake; single- or multi-perforated cylinder	NC, diphenylamine
Double base	M2	Single- or multi-perforated cylinder	NC, NG, ethyl centralite
	M5	Single-perforated cylinder or flake	NC, NG, ethyl centralite
	M8	Increment sheet	NC, NG, diethylphthalate
Triple base	M30	Multi-perforated cylinder or hexagonal	NC, NG, NQ, ethyl centralite
	M31	Multi-perforated cylinder; Single-perforated cylinder or stick	NC, NG, NQ, ethyl centralite

<sup>1</sup> Particles shapes are shown in Figure 1-1.

Three of the stabilizers utilized in propellant formulations are diphenylamine (DPA), ethyl centralite (diethyl diphenyl urea), and akardites (methyl diphenyl urea). DPA is used only in single-base propellants because it is incompatible with the gelatinizing agent NG. Double- and triple-base propellant formulations with NG use either ethyl centralite or 2-nitrodiphenylamine as a stabilizer. Some double- and triple-base compositions that employ diethylene glycol dinitrate (DEGDN) rather than NG as the gelatinizer use a form of akardite for stabilization.

Deterrents or burn rate modifiers are added to propellants used in small arms and large-caliber artillery rounds. They are impregnated into the propellant surface, forming a coating that slows the initial burning rate. Commonly used deterrents include 2,4-dinitrotoluene (DNT), 2,6-dinitrotoluene, and ethyl centralite. A variety of alkali metal salts also are added to some propellants to help reduce secondary flash and smoke.

Other non-energetic binders and plasticizers are included in some propellant compositions to make the grains less brittle. Examples are two esters of 1,2-

benzenedicarboxylic (or phthalic) acids—dibutyl phthalate and diethyl phthalate. A less commonly used binder is triacetin.

The propellant grains are also often coated with graphite, a lubricant that prevents the grains from sticking together and dissipates static electricity, avoiding undesired ignitions. Other additives can be included to lower wear of the gun barrel liners. Examples include wax, talc, and titanium dioxide.

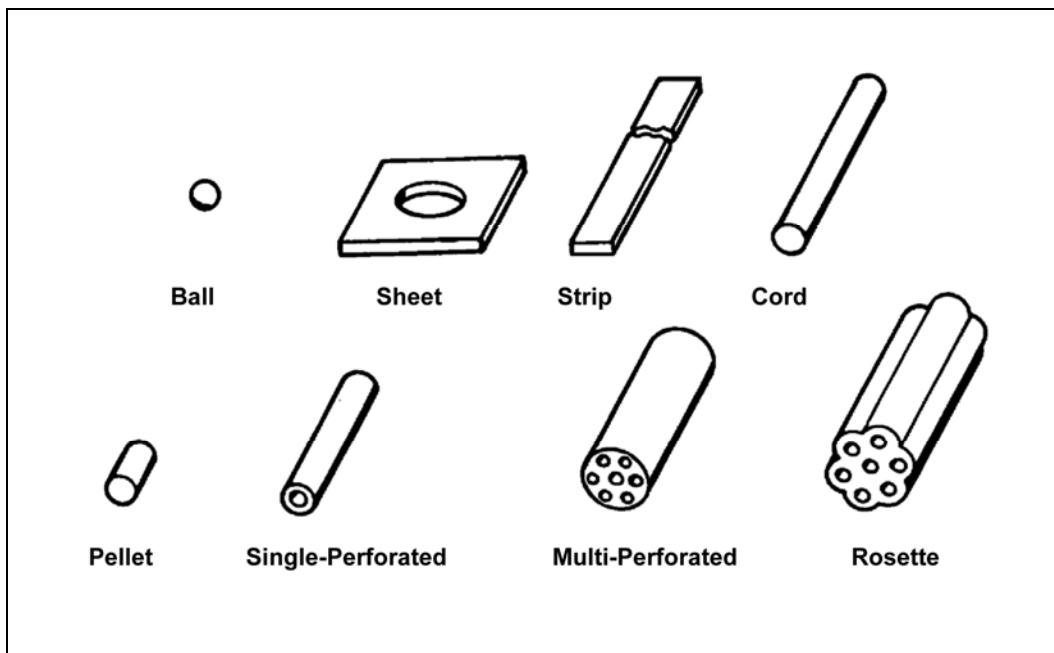
### **Grain size and shape**

The properties of the propellant are greatly influenced by the size and shape of the grains, which can be in a variety of small spherical balls, plates, or flakes, or in different forms of extruded cylinders (Fig. 1-1). The propellant burns only on the particle surfaces; therefore, larger grains burn more slowly. Many of the cylindrical shapes have internal perforations to allow burning from the inside outwards simultaneously with burning from the outside inwards. Some cylinders have a single central perforation; others have multiple perforations, commonly with a central hole surrounded by six others. The size and shape of propellant grains used in a particular munition are balanced in an attempt to regulate the burn so that an evenly constant pressure is exerted on the propelled projectile while it is in the barrel.

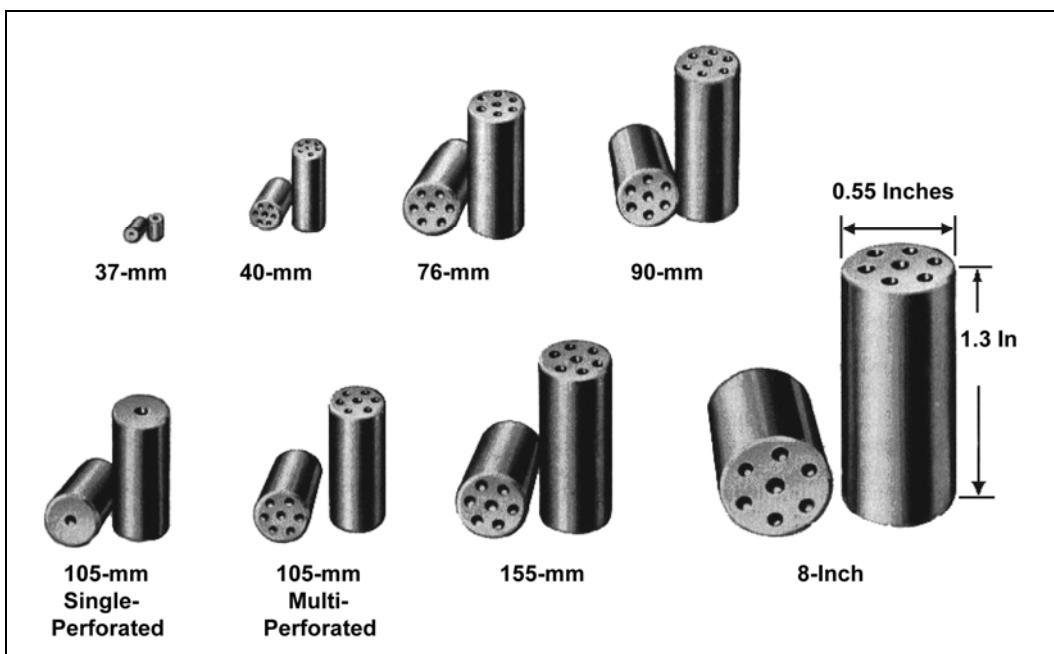
### **Ignition train**

Propelling charges are ignited through a chain reaction called an ignition train, usually a series of combustibles and explosives arranged according to decreasing sensitivity (Fig. 1-2). To activate, a stimulus such as impact, heat, or spark ignites a small primer. In artillery ammunition, the primer then sets fire to the igniter charge, which intensifies the small flame produced by the primer and initiates combustion of the large quantity of propellant. In some cases, igniter charges also are sandwiched between layers of propellant. Commonly used igniter charges include black powder—a combination of potassium nitrate, charcoal, and sulfur—and potassium nitrate by itself.

Primer compositions are a mixture of primary explosives, fuels, oxidizers, and other binders. Primary explosives include lead azide, diazodinitrophenol (DDNP), lead styphnate, tetracene, potassium dinitrobenzofuroxane (KDNBF), and lead mononitroresorcinate (LMNR). Fuels used are thiocyanate, antimony sulfide, and calcium silicide. Oxidizing agents include potassium chlorate and barium nitrate.

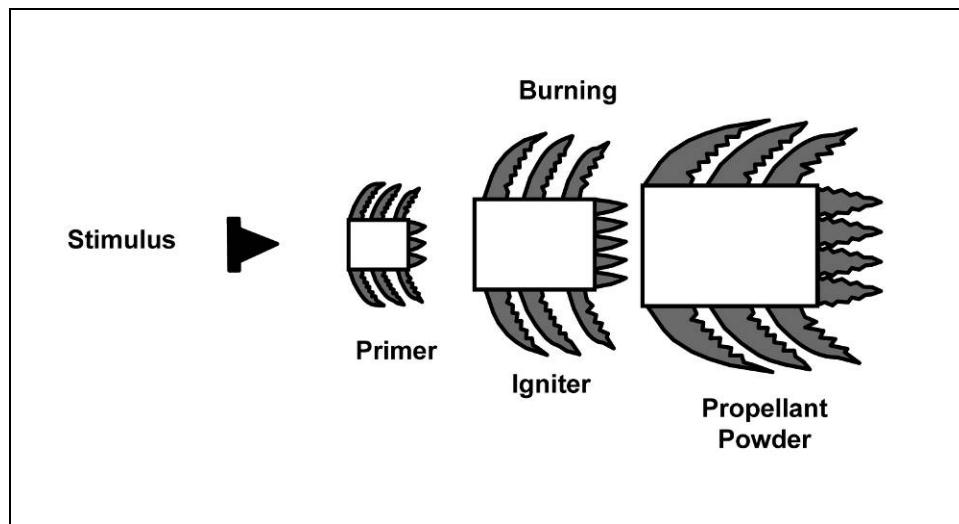


a. Propellant grain shapes.



b. Example sizes.

Figure 1-1. Propellant grain shapes and example sizes. (From U.S. Army 1990, 1993.)



**Figure 1-2. Schematic of propelling charge ignition train. (From U.S. Army 1990.)**

Primers include three main types: percussion, stab detonator, and electrical. Several percussion and stab detonator priming compositions include the compounds lead styphnate, tetracene, barium nitrate, antimony sulfide, powdered zirconium, lead dioxide, and PETN.

The most commonly used electrical primers are the exploding bridge wire, the hot wire bridge, and the film bridge. In an exploding wire detonator, a large current passing through the wire causes it to burst, creating a shock wave that causes the detonation. With this type, no priming composition is needed; the wire is placed directly in a charge of RDX or PETN. Hot wire and film bridges use priming compositions that include potassium chlorate with various combinations of lead mononitroresorcinate, NC, lead thiocyanate, DDNP, charcoal, nitrostarch, titanium, and aluminum.

### Summary

Table 1-2 summarizes the significant ingredients that compose the propellant portion of propelling charges. The greatest mass is composed of the oxidizers and energetic binders, ranging between 60 and 90 percent by weight (Ase et al. 1985, Ross et al. 1988, Kirchner et al. 1993, Leib and Heimerl 1994, Miller 1997, Yazici et al. 1998, MIDAS 2006, Mirecki et al. 2006). Plasticizers and inert binders account for approximately 5 to 25 weight percent. Stabilizers and other compounds (flash reducers, primers, and igniters) account for the remainder, occurring at less than 5 weight percent each.

**Table 1-2. Significant compounds in propellant formulations.**

Oxidizers and energetic plasticizers	Stabilizers	Inert binders and plasticizers	Other
<b>Nitro-base</b>	diphenylamine	dibutyl phthalate	<b>Burn rate modifiers</b>
nitrocellulose	2-nitrodiphenylamine	diethyl phthalate	2,4-dinitrotoluene
nitroglycerin	ethyl centralite	triacetin	2,6-dinitrotoluene
nitroguanidine	akardite	wax	ethyl centralite
diethylene glycol dinitrate		talc	<b>Flash reducers</b>
<b>Other</b>		titanium oxide	potassium sulfate
ammonium perchlorate			potassium nitrate
potassium perchlorate			

### *Larger rocket propellants*

Composite propellants, typically used in medium and large rocket motors, contain neither nitrocellulose nor an organic nitrate. They generally consist of a physical mixture of an organic fuel (such as ammonium picrate), an inorganic oxidizer (commonly perchlorate or aluminum), and an organic binding agent. These mixtures have adequate mechanical strength to be manufactured in dimensions larger than NC-base propellants, making them favorable for use in larger rocket motors.

### **Previous research on propellant residues at military ranges**

The first documented results for propellant residues in soil were from samples collected at Explosives Ordnance Disposal (EOD) ranges in Alaska and Mississippi. During an investigation of the reason for a series of waterfowl deaths at Eagle River Flats, an artillery impact area at Fort Richardson, Alaska, Racine et al. (1992) analyzed sediments collected near an EOD range and reported detecting 2,4-DNT, a component of M1 propellant used with 105-mm howitzers. These samples and several others from an EOD range at Camp Shelby, Mississippi, were further analyzed by GC/MS and found to contain not only 2,4-DNT, but also diphenylamine and dibutyl phthalate, also ingredients of M1 propellant (Walsh and Jenkins 1992). Similarly, Phillips and Bouwkamp (1994) found nitroglycerin, 2,4-DNT, n-nitrosodiphenyl amine, and dibutyl phthalate in soil samples collected from firing point areas at Aberdeen Proving Ground, Maryland. N-nitrosodiphenyl amine is a product formed from the reaction of nitrogen oxides (released from decomposition of NC during storage of M1 propellants) and diphenylamine (Folly and Mäder 2004).

A series of investigations at impact areas and firing point areas was sponsored by U.S. Army Environmental Center (AEC), SERDP (ER-1155), the National Guard Bureau at Massachusetts Military Reservation (MMR), U.S. Army Alaska, and the Canadian Government by the Department of National Defence Canada.

The AEC program sampled artillery firing point areas at Camp Shelby, Mississippi; Fort Bliss, New Mexico; Fort Polk, Louisiana; Fort Hood, Texas; and Fort Carson, Colorado. At Camp Shelby, AEC found 2,4-DNT, 2,6-DNT, and NG at one of two firing point areas that were sampled (USACHPPM 2001). Similarly, two artillery firing points were sampled at Fort Bliss. NG was the only propellant-related compound that was detected at one firing point at the sub mg/kg level, but it was not found in soil samples from the second firing point area. Results from the AEC study at Fort Carson have not been published, but CRREL sampled the same firing point areas as a part of SERDP ER-1155. Analytical results indicated that NG was present in surface soils at firing point 141 at concentrations ranging from 8.5 to 20.6 mg/kg (Hewitt, unpublished results).

A series of studies sponsored by U.S. Army Alaska investigated the levels of propellant residues at firing points and impact areas at Fort Richardson and Fort Greely, Alaska. In the initial study, two types of firing points were sampled: an area where 1800 40-mm grenades were fired for a special test, and a firing point at Lampkin range used for firing a number of weapon systems including mortars and 105-mm howitzers (Walsh et al. 2001). M2 propellant is used for 40-mm grenades and contains nitroglycerin; an empty cartridge case found at this site contained NG (650 µg). No energetic residues were found in soils at this firing point; the likely reason for this was because it is located within the active floodplain of the Delta River in an area with evidence of recent erosion. At the Lampkin firing point, both NG and 2,4-DNT were found in surface soils. The concentration of NG in two samples was 3.3 and 16.5 mg/kg; the measured 2,4-DNT concentrations were only 0.005 and 0.044 mg/kg.

Subsequent studies concentrated on 105-mm howitzer firing points at the Donnelly Training Area (formerly Fort Greely). Extensive sampling was conducted at both vegetated and unvegetated firing points. Concentrations of 2,4-DNT varied widely but were generally in the low mg/kg range. Experiments indicated that residues were deposited at least 100 m from the muzzle of the 105-mm howitzers (Walsh et al. 2004). Additional research indicated that the propellant residues were deposited as particulate matter, most likely fibers of burned and unburned propellant (Walsh et al. 2004). Multi-increment samples composed of at least 50 increments were found to provide representative samples for areas

as large as 10,800 m<sup>2</sup>. Accurate estimation of the 2,4-DNT concentration in these samples required that either the entire sample had to be extracted or the sample had to be ground thoroughly before it could be reproducibly subsampled. Concentrations of 2,4-DNT in the low mg/kg also were found for 105-mm firing points at Fort Richardson (Walsh et al. in prep).

The largest number of soil samples collected at any training range has been at Camp Edwards, Massachusetts Military Reservation, on Cape Cod. Clausen et al. (2004) summarized the results from this study for gun and mortar firing points. 2,4-DNT was detected in 4% of the soil samples collected at this range, mostly in the surface to 1-ft-depth samples. Also, 2,6-DNT, diethyl phthalate, N-nitrosodiphenylamine, and di-n-butyl phthalate were occasionally found. In addition, 2,4-DNT and NG were found on the KD rocket range (Ogden 2000).

As a part of SERDP ER-1155, a number of firing point areas were sampled. Antitank rocket firing points were sampled at Yakima Training Center (Pennington et al. 2002), CFB-Valcartier (Jenkins et al. 2004), CFB-Gagetown (Thiboutot et al. 2004), and CFB-Petawawa (Brochu et al. 2006). In all cases, NG was found in front, and to a much greater extent, behind the firing line, where the shoulder-fired anti-tank rockets are fired. Concentrations as high as 2400 mg/kg have been found in surface soils and NG deposition has been detected at least 25 m behind the firing line.

Artillery firing points also were sampled at Fort Lewis, Washington, and Yakima Training Center, Washington. At Fort Lewis, 2,4-DNT was detected in surface samples in front of a firing position where 105-mm howitzers had fired more than 600 rounds in the proceeding month (Jenkins et al. 2001). At Yakima, samples were collected at the multi-purpose range complex at a fixed firing position where 120-mm tank cannons were fired. Both 2,4-DNT and NG were detected as far as 75 m in front of the firing position (Pennington et al. 2002).

## Scope of project

This project was designed to acquire data for estimating mass and concentrations of propellant residues in the source zone, as well as process descriptors for mass transport from the surface to groundwater or in runoff—the data needed for use in risk assessments. Another objective is to evaluate actual ground-truth of propellant transport at specific sites.

The study was executed in several thrust areas. The first involved quantifying the amounts of burned combustion products being emitted during an individual firing of various gun and rocket types, including both gaseous emissions and particulate residues. Field experiments were conducted during live-fire training

of various weapons to delineate the footprint of deposition and mass deposited as a function of distance from the firing position. Winter trials utilized pristine snow surfaces for collection of samples to estimate mass. In summer trials, we used witness plates or small pans to collect residue for mass estimation and microscopic analysis. These studies will be described in Chapters 2 and 3.

A second thrust involved collecting representative soil samples at several training ranges to assess the accumulation rate of propellant residues for the different weapons systems. A portion of this work involved an effort to refine sampling, subsampling, and analytical protocols that were developed in ER-1155 for explosives residues, to accommodate the determination of propellant residues, particularly for those containing ammonium perchlorate and NQ. This research will be described in Chapters 3, 4, and 6.

The third thrust involved using laboratory column experiments to define transport process descriptors suitable for use in environmental transport models and/or in environmental and human health risk assessments. Selected propellant constituents and solid-phase propellant formulations were tested under different flow regimes and in different soils. Results will be described in Chapter 5.

## **Objectives**

The two major objectives of SERDP ER-1481 are

1. Develop the environmental data to characterize potential releases and fate of gun and rocket propellants as they occur on training and testing ranges.
2. Characterize residues from gun propellants and characterize leaching rates of contaminants bound in these materials.

In addition to general propellant distribution and characterization, investigations are ongoing to fill specific data gaps.

1. No data exist on deposition of perchlorate during the firing and propulsion of the various types of military rockets, yet anticipated new environmental regulations establishing a perchlorate limit in drinking water requires DoD to thoroughly understand its environmental life cycle. Results of this study will define perchlorate occurrence and distribution.
2. Results of soil-to-water partitioning tests suggest that NQ, the major component of certain triple-base propellants, is persistent and mobile in the environment (Brannon et al. 2004, Mulherin et al. 2005). However, monitoring activities typically have ignored NQ (Clausen

et al. 2004). Therefore, our characterization studies will assess the need to monitor for NQ and provide procedures for characterizing NQ residues.

3. All gun and mortar propellant residues contain high percentages of nitrocellulose, but its persistence on ranges is unknown. NC has been found in the percent level behind the firing line at antitank rocket ranges (Jenkins et al. 2004, Thiboutot et al. 2003, Brochu et al. 2006), but its origins and distribution are not well characterized.
4. Spain (1995) has developed a thorough understanding of the mechanisms of 2,4-DNT mineralization in bioremediation matrices, but it is uncertain whether these mechanisms are operational for the much lower concentrations present in training range soils (Jenkins et al. 2001, Pennington et al. 2001, Walsh et al. 2004).

## References

**Ase, P., W. Eisenberg, S. Gordon, K. Taylor, and A. Snelson** (1985) Propellant combustion product analyses on an M16 rifle and a 105-mm caliber gun. *Journal of Environmental Science and Health* A20(3):337–368.

**Brannon, J.M., C.B. Price, S.L. Yost, C. Hayes, J.W. Mirecki, and B. Porter** (2004) Fate and transport parameters for firing range residues. In *Distribution and fate of energetics on DoD test and training ranges: Interim Report 4*. ERDC TR-04-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Brochu, S., E. Diaz, S. Thiboutot, G. Ampleman, A.D. Hewitt, S.R. Bigl, M.E. Walsh, K. Bjella, T. Ranney, M.R. Walsh, S. Taylor, C. Ramsey, D. Lambert, and N. Perron** (2006) Assessment of 100 years of military training in Canada: The case of Canadian Force Base Petawawa. In *Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 6*. ERDC TR-06-12. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Clausen, J., J. Robb, D. Curry, and N. Korte** (2004) A case study of contaminants on military ranges: Camp Edwards, Massachusetts, USA. *Environmental Pollution* 129:13–21.

**Folly, P., and P. Mäder** (2004) Propellant Chemistry. *CHIMIA International Journal for Chemistry* 58(6):374–382.

**Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and Major E. Wahlgren** (2001) *Characterization of Explosives Contamination at Military Firing Ranges*. ERDC TR-01-05. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, and K.L. Bjella** (2004) *Representative Sampling for Energetic Compounds at an Antitank Firing Range*. ERDC/CRREL TR-04-7. Hanover, NH: U.S. Army Engineer Research and Development Center.

**Kirchner, D.B., J.C. Gaydos, and M.C. Battigelli** (1993) Combustion products of propellants and ammunition. In *Occupational Health—The Soldier and the Industrial Base*. Deeter, D.P., and Gaydos, J.C., eds., Office of the Surgeon General, Walter Reed Medical Center, Washington DC, 359–396.

**Lieb, R.J., and J.M. Heimerl** (1994) *Characteristics of JAX Gun Propellants*. ARL-TR-465, AMSRL-WT-PA, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD.

**MIDAS** (Munitions Items Disposal Action System) (2006) Defense Ammunition Center, McAlester, OK (<https://midas.dac.army.mil/>).

**Miller, M.S.** (1997) *Thermochemical Properties of Six Solid Gun Propellants*. ARL-TR-1322. Army Research Laboratory, Aberdeen Proving Ground, MD.

**Mirecki, J.E., B. Porter, and C.A. Weiss, Jr.** (2006) *Environmental Transport and Fate Process Descriptors for Propellant Compounds*. ERDC/EL TR-06-7. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Mulherin, N.D., T.F. Jenkins, and M.E. Walsh** (2005) *Stability of Nitro-guanidine in Moist, Unsaturated Soils*. ERDC/CRREL TR-05-2. Hanover, NH: U.S. Army Engineer Research and Development Center.

**Ogden** (2000) *Final IAGS Technical Team Memorandum 99-1 KD & U Ranges for the Camp Edwards Impact Area Groundwater Quality Study, Massachusetts Military Reservation Cape Cod, Massachusetts (MMR-1903)*, July 2000. Report prepared for the National Guard Bureau. Westford, MA: Ogden Environmental and Energy Services.

**Pennington, J.C., T.F. Jenkins, J.M. Brannon, J. Lynch, T.A. Ranney, T.E. Berry, Jr., C.A. Hayes, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, and J.J. Delfino** (2001) *Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 1*. ERDC TR-01-13. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, D. Lambert, J. Clausen, and J.J. Delfino** (2002) *Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2*. ERDC TR-02-8. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Phillips, L.F., and C.A. Bouwkamp** (1994) *Wastewater Management Study No. 32-24-HP16-94. Effects of Active Firing Range Activities on Environmental Media. Aberdeen Proving Ground–Aberdeen Area, Maryland, 31 January–30 November 1993*. Aberdeen Proving Ground, MD: U.S. Army Environmental Hygiene Agency.

**Racine, C.H., M.E. Walsh, C.M. Collins, D.J. Calkins, B.D. Roebuck, and L. Reitsma** (1992) *Waterfowl Mortality in Eagle River Flats, Alaska: The Role of Munitions Residues*. CRREL Report 92-5. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory.

**Ross, R.H., B.C. Pal, R.S. Ramsey, R.A. Jenkins, S. Lock, W.H. Griest, and M.R. Guerin** (1988) *Problem Definition Study on Techniques and Methodologies for Evaluating the Chemical and Toxicological Properties of Combustion Products of Gun Systems*. 1, AD-ORNL-6334/V1, (ADA091290). Oak Ridge, TN: Oak Ridge National Laboratory.

**Spain, J.C.** (1995) Bacterial degradation of nitroaromatic compounds under aerobic conditions. In *Biodegradation of Nitroaromatic Compounds*. J.C. Spain, Ed., 19–35. New York: Plenum Press.

**Thiboutot, S., G. Ampleman, A. Hamel, J.M. Ballard, R. Martel, R. Lefebvre, and S. Downe** (2003) *Research on the Environmental Conditions of Ground and Surface Water Prevailing in the Training Area at CFB Gagetown, New Brunswick*. DRDC Valcartier TR 2003-016. Québec, Québec: Defence Research and Development Canada–Valcartier.

**Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, K. Bjella, C. Ramsey, and T.A. Ranney** (2004) *Environmental Conditions of Surface Soils, CFB Gagetown Training Area: Delineation of the Presence of Munitions-Related Residues (Phase III, Final Report)*. DRDC Valcartier TR 2004-205. Québec, Québec: Defence Research and Development Canada–Valcartier.

**USACHPPM** (2001) *Final Geohydrologic Study No. 38-EH-6807-02. Training range site characterization and risk screening, Camp Shelby, Mississippi, 7–23 September 1999*. Aberdeen Proving Ground, MD: U.S. Army Center for Health Promotion and Preventive Medicine.

**U.S. Army** (1990) *Military explosives*. Department of the Army, Headquarters, Washington, D.C., Army Technical Manual TM 9-1300-214 (with Change No. 4).

**U.S. Army** (1993) *Ammunition, general*. Department of the Army, Headquarters, Washington, D.C., Army Technical Manual TM 9-1300-200 (with Change No. 5).

**Walsh, M.E., and T. Jenkins** (1992) *Identification of TNT Transformation Products in Soil*. CRREL Special Report 92-16. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory.

**Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney** (2001) *Sampling for Explosives Residues at Fort Greely, Alaska: Reconnaissance Visit July 2000*. ERDC/CRREL TR-01-15. Hanover, NH: U.S. Army Engineer Research and Development Center.

**Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T.S. Douglas, N. Perron, D. Lambert, R. Bailey, and K. Myers**  
(2004) *Range Characterization Studies at Donnelly Training Area, Alaska: 2001 and 2002*. ERDC/CRREL TR-04-3. Hanover, NH: U.S. Army Engineer Research and Development Center.

**Walsh, M.E., C.M. Collins, C.A Ramsey, and others** (in prep) *Energetic Residues on Alaskan Training Ranges: Studies in 2005 and 2006*. ERDC/CRREL Technical Report. Hanover, NH: U. S. Army Engineer Research and Development Center.

**Yazici, R., D.M. Kalyon, and D. Fair** (1998) *Microstructure and mixing distribution analysis in M30 triple-base propellants*. Picatinny Arsenal, PA: U.S. Army Armament Research, Development and Engineering Center.

## **2 Energetic Residues Deposition from 60-mm and 81-mm Mortars**

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### **Introduction**

Military live-fire training missions utilize a variety of energetic materials. In the case of mortars, cartridges are issued with various types and configurations of propellants, depending on the type and age of the round. These energetic materials are never completely consumed during firing and have the potential to accumulate on military training ranges where they are used (Pennington et al. 2002, Hewitt et al. 2003, Jenkins et al. 2005). In January 2006, CRREL teamed with the 1st Battalion, 501st Parachute Infantry Regiment (PIR) in Alaska to sample areas used during a mortar training mission. The objectives of this field work were to examine mass loadings at firing points for 60-mm and 81-mm mortars during a live-fire exercise, to obtain controlled baseline data on mortar propellant residues at burn points, and to obtain impact area data for point-detonating 60-mm high-explosive rounds.

### **Background**

The examination of firing points as a source of energetic residues is a recent thrust in range sustainability research. Studies funded by U.S. Army Alaska (Soil and Water Quality Monitoring Fund) at Fort Wainwright's Donnelly Training Area (DTA) starting in 2000 (Walsh et al. 2001) indicated propellant-related energetic compounds were accumulating at heavily used firing points. Further research in 2001 and 2002 (Walsh et al. 2004) reinforced the original indications, with the propellant constituents nitroglycerin (NG) and 2,4-dinitrotoluene (2,4-DNT) recovered at several firing points. The State of Alaska lists 2,4-DNT as a hazardous substance. Burn points, areas where excess propellants are burned off following training exercises, had unreacted residues at concentrations several orders of magnitude higher than at firing points, primarily of 2,4- and 2,6-DNT.

Although significant, these findings were only preliminary and much ground-breaking work on sample collection and processing was required. Sample collection was slow and difficult, with a variety of soils and levels of vegetation to deal with. A sample design that gave consistent results was needed, and a method of

processing the samples so that subsamples were replicable had to be worked out. These technical issues have been resolved, and we hypothesized that the methods developed would be transferable to other sampling applications.

In 2002, SERDP funded research at Fort Richardson in Alaska to estimate residue deposition from the detonation of 105-mm and 81-mm high-explosive (Composition B) projectiles. Following the firing of the 105-mm howitzers, residues were collected from the snow-covered area in front of one of the guns. Preliminary results indicate concentrations of propellant residues much higher than found at the impact areas (Hewitt et al. 2003, Walsh et al. 2004, Walsh et al. 2005b, Ramsey et al. in prep.).

The ease of sample collection on snow and the processing of these samples led us to consider further work on winter firing point sampling as an adjunct to the impact area work we were then conducting for SERDP. The methodology for the collection of samples on snow originally developed by Jenkins et al. (2000a, 2002) was optimized by Walsh et al. (2005a), making sampling much more efficient and repeatable. Leveraging funding from both SERDP and U.S. Army Alaska allowed us to sample active firing points and burn points for 120-mm mortars and the 155-mm howitzer to further this preliminary investigation (Walsh et al. 2005b, 2005c). Results from these tests demonstrated that firing points and burn points are areas of concern for range sustainability and maintenance.

The accumulated information led to the submission of a proposal to SERDP to formally investigate military range firing points. The tests documented here, conducted in cooperation with the U.S. Army at Fort Richardson, Alaska, are both a continuation of the previous work cited above and a fresh start on the new research program targeted at providing reliable estimates of propellant residue deposition at firing points for a variety of weapon systems. With this information, better range maintenance and improved range sustainability for the U.S. military will be possible.

## **Field Tests**

### *Field Site*

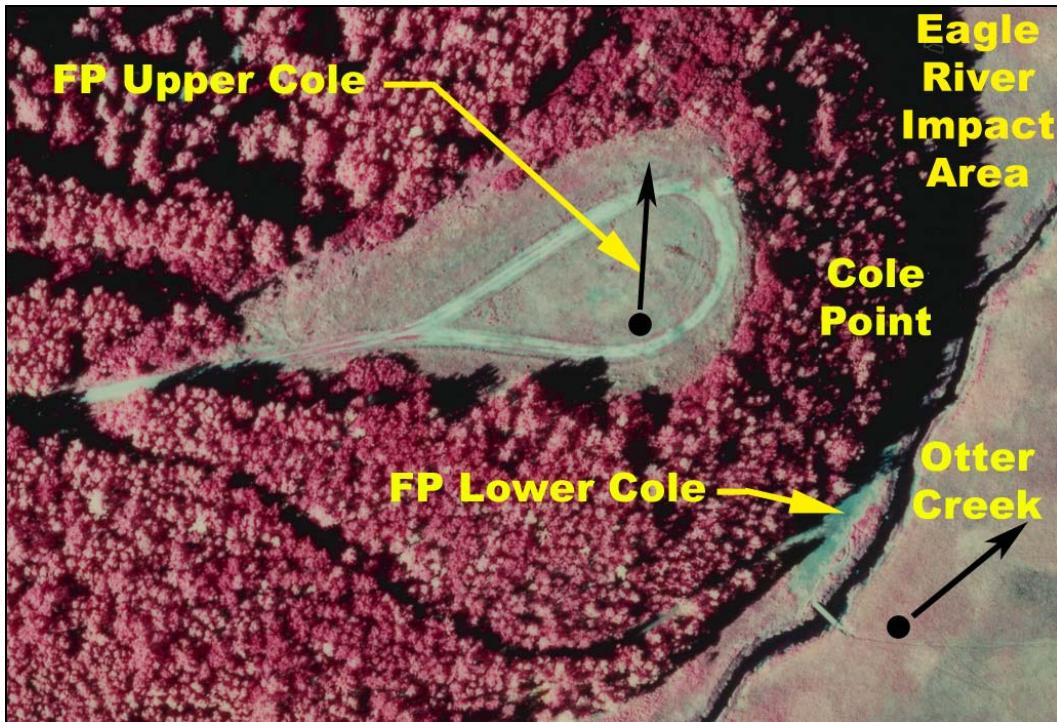
The tests were conducted at the Eagle River Flats Range, Fort Richardson, Alaska. Eagle River Flats (ERF) is an estuarine salt marsh along the upper Cook Inlet that periodically floods and freezes over the course of the winter, building up layers of ice over the impact area (Fig. 2-1). With a fresh layer of snow on the ice, this area is ideal for conducting explosives residues tests as the impact

detonation plumes are segregated from past activity on the Flats and residues are easily discerned on the snow surface. The Flats were used to collect the samples for the 60-mm impact points.



**Figure 2-1. Eagle River Flats impact area from Firing Point Upper Cole.**

At the southwest corner of the Flats lies Cole Point. Cole Point encompasses two firing points, Upper Cole and Lower Cole (Fig. 2-2). Upper Cole is located on a bluff overlooking Eagle River Flats. It is a 0.4-ha open area used as a bivouac area and observation point as well as a firing point. Firing points for two 81-mm and one 60-mm mortar were established in this area. Burn points also were set up here. Lower Cole is located along the southeastern base of the Cole Point bluff slightly above the Flats. It is a small area that is not suitable for use as a firing point. A small footbridge crosses the adjacent Otter Creek, allowing access to the Flats. It was in this area, about 50 m from Lower Cole, that the second firing point for the 60-mm mortars was established.



**Figure 2-2. Cole Point area and firing points (●). Arrows indicate direction of fire.**

At the time of these tests daytime temperatures ranged from  $-22^{\circ}\text{C}$  to  $-12^{\circ}\text{C}$ . Winds were calm to variable from the north at under 0.7 m/sec with partially overcast skies. Thick ice fog enveloped the area when winds diminished. Snow depth at the firing points ranged from 25 to 35 cm. In the impact area, snow depth ranged from 2 to 20 cm over ice with a thickness of up to 80 cm. No liquid water resided in the impact area where we sampled the detonation plumes. A light snow fell overnight on the 18th through the morning of the 19th of January 2006, with an accumulation of  $\approx 10$  cm. There were about six hours of daylight each day.

#### *Munitions*

Three types of munitions were fired during our tests (Table 2-1). The 60-mm test munitions were M888 high-explosive (HE) cartridges with an M935 point detonating (PD) fuze mounted in the nose (Fig. 2-3a). For the 81-mm tests, the M374A3 HE cartridge with an M567 PD fuze (Fig. 2-3b) and the M301A3 illumination cartridge with an M84A1 time fuze were fired. The M374A3 cartridge uses an M205 single-base charge (M10) primarily composed of nitrocellulose (NC). The M301A3 cartridge uses an M185 double-base charge

(M9) composed primarily of NC and nitroglycerin (NG). The Army's Propellant Management Guide (1998) formulation for the 60-mm M888 propellant charge (M204) lists the M10 formulation as containing NC at 84.2% (6.8 g) and DNT at 9.9% (0.8 g). This differs from the M10 formulation for the M205 propelling charge for the M374A3 round. Both MIL-P-63194A (M204) (U.S. Army 1981) and MIL-P-48130A (M205) (U.S. Army 1982) refer to MIL-STD-652 (U.S. Army 1969) for the M10 propellant composition. Grains of raw propellant for both charges were analyzed and DNT was not detected in either. The MIL-STD-652C formulation (98% NC) is thus shown for the M204 charge in the table below. All cartridges have additional quantities of energetics (NC and NG) in the ignition cartridges located in the tail assemblies that either propel the round ("zero" charge) or ignite the added propellant charges. The amount of propellant charges used with each round varied, depending on the training requirement.

**Table 2-1. Propellant constituents for munitions used during firing point tests.**



a. 60-mm cartridge.



b. 81-mm cartridge.

**Figure 2-3. High-explosive rounds used in tests.**

During previous SERDP-funded research, we examined detonation residues from several common military munitions. One of the munitions families for which we lacked reliable data was the 60-mm mortar. Given the opportunity presented during this field research, we added sampling of the detonation plumes of 60-mm HE rounds to our list of tasks. The M888 HE round contains 358 g of Composition B high explosive (Comp B) in the projectile body consisting of 215 g of RDX and 140 g of TNT. The M935 PD fuze adds 15 g of RDX to the explosive load. Appendix A contains complete munitions data for these tests.

### Tests

Our tests were conducted in association with a training mission being conducted by the 1/501st PIR. Coordinating with the mission command, we located firing positions for one of two M252 81-mm mortars at Upper Cole. We flagged off an area approximately 35 m out in the direction of fire to restrict traffic in the area we anticipated sampling. We also designated a firing position at Lower Cole for the M19 mortar. The area in front of this firing position was flagged off downrange for sampling.



**Figure 2-4. M19 mortar and M888 cartridge with a single M204 propellant charge.**

The 60-mm tests were run first. The M19 mortar is a light, handheld mortar used for close-in support (Fig. 2-4). The maximum number of propellant charges on an M888 round that can be used with this weapon is two. For our test, the mortar squads cycled through the firing position firing rounds at close-in targets with either “zero” charge (using the ignition cartridge in the tail to propel the

round) or a single M204 propellant charge. The number of rounds fired and the total number of M204 charges used were tracked. An intermittent wind of 0.7 m/s was blowing downrange from behind the mortar squads.

Following the completion of the training for the first group of mortar squads, we sampled the area in front of the position. The propellant residue plume was estimated using visible residues and ejected obturator rings to approximate its bounds. The plume was marked and recorded via GPS (Trimble GPS Pathfinder Pro XR,  $\pm 1\text{-m}$  accuracy) by walking around it. Demarcated sampled areas, or decision units, at 15 m, 25 m, 35 m, and 50 m were flagged downrange of the position for additional sampling. Trays to collect propellant debris for another research project that had been placed in front of the position, visible in Figure 2-4, were collected. The snow was then sampled for residues. The sampling method will be covered in the next section.

The 81-mm tests were not as straightforward. The space at FP Upper Cole was limited, with two gun positions, the ammunition storage area, the bivouac for the troops, and parking for vehicles all in a limited area. The crowding limited our ability to designate a generous “clean” area for sampling, but the troops were accommodating to the extent possible. The range of the M252 81-mm mortar (Fig. 2-5) is farther than for the small M19 mortar, requiring the ability to see far downrange to spot the impacts. Low temperatures and a lack of wind contributed to the formation of ice fog, delaying training until just before nightfall on 18 January. With the firing of a few spotting rounds and the sighting in of the weapons, night fell and a light snow started. We departed for the day while the squads practiced their firing with illumination rounds.



**Figure 2-5. M252 mortar and M374A3 cartridge with two M205 propellant charges.**

When we returned the following morning, training had been delayed further by the darkness and the snow, but the squad leaders had tracked the number of rounds and charges used throughout the training exercise. Upon completion of firing, we retrieved the collection trays, marked the decision units as outlined above, and sampled these areas for residues.

For the burn tests, we collected 20 excess charges from each of the three munitions to burn in piles of ten. These piles were located and recorded in an area of low residues 30 m downrange of the test mortar position. Both piles for each propellant type were ignited and allowed to burn out (Fig. 2-6).

The final test was run during the waning hours of 19 January. An M224 60-mm mortar system was used to fire 10 M888 HE rounds into an area designated in the Eagle River Impact Area. The rounds were fired with two M204 propellant charges each. Eight of the 10 rounds detonated. Following the cessation of firing, an EOD specialist from the 716th EOD detachment from Fort Richardson (Bradley) located the dudded rounds and cleared the remaining area. We then drove out to the impact plumes with our sampling equipment. The plumes were demarcated by walking outside the visible area of residues. The outlined plumes were recorded with a GPS unit. Five single-impact plumes and one double-impact plume were sampled. The eighth detonated round landed among some river ice blocks and was not sampled. In the fading light of the afternoon, we were not able to conduct all the quality assurance sampling we had planned. Sampling is described in the next section.



a. Burning propellant charges.

Figure 2-6. Propellant burn test (M204 charges).



**b. Residue from charges**

**Figure 2-6 (cont'd). Propellant burn test (M204 charges).**

#### *Sampling Method*

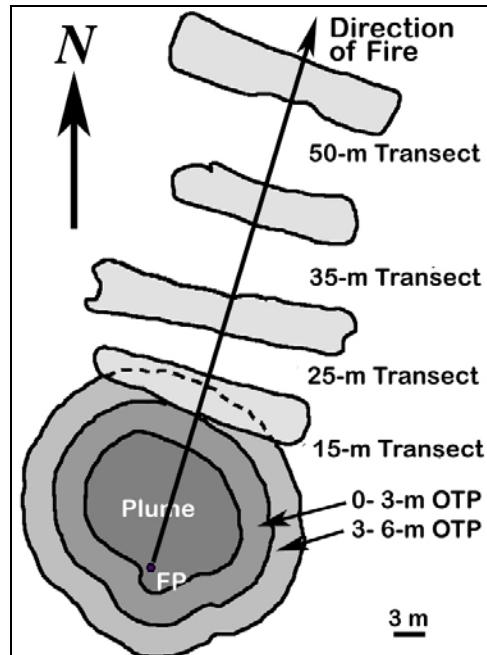
Sampling was done on a fresh snow surface following the protocol established by Walsh et al. (2005a). Briefly, 40 to 100 increments of surface snow are collected within a decision unit (inside the demarcated plume, outside the plume, at depth beneath previously sampled points, etc.), until the decision unit is representatively sampled. The increments for a given sample are collected in a single clean polyethylene bag to make up a multi-increment sample (MIS). Triplicate sampling allowed us to test and compensate for uncertainty derived from the small total area collected from within each decision unit, generally less than 1 m<sup>2</sup>.

To estimate the mass of energetic residues, we need to know the area over which the energetic material is deposited and the average concentration for that area. A critical assumption is that the plume represents the major area of deposition. The plume is composed of deflagration or detonation products and its depositional pattern can be affected by wind. However, because there is no other way to estimate the area of deposition, we assume that most HE residues are deposited within the plume and tested this assumption by taking multi-increment samples in concentric annuli around the outside of the plume (OTP). The objectives of OTP sampling are to ensure that the plume was adequately outlined and to determine how much, if any, of the unconsumed energetics are measurable outside of the plume. Samples were obtained for annuli at varying distances (0–3 and 3–6 m) surrounding the plume edge.

Additional quality control work was done within some of the plumes. Sub-surface samples were taken beneath the sample locations to test whether we were sampling deep enough to recover all the residues. Two tests also were run to determine how much influence individual samplers have on residues recovery.

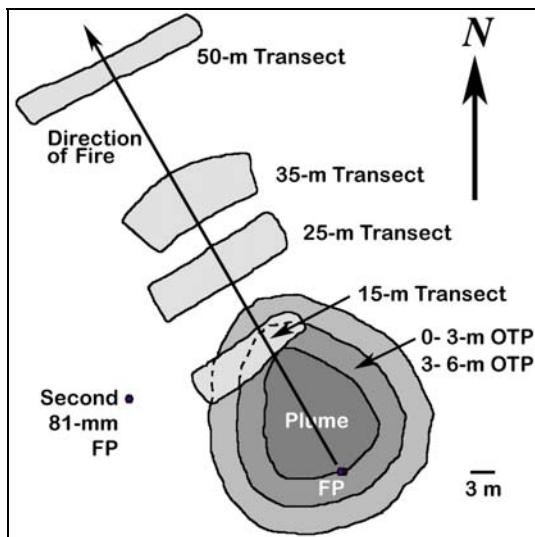
Teflon-lined aluminum scoops are used to obtain either a 10-cm- $\times$ 10-cm- $\times$ 2-cm-deep volume of snow or a 15-cm- $\times$ 15-cm- $\times$ 2-cm-deep volume of snow. Sampling depth is normally 1 cm, but because of the loose, low-density surface snow we sampled deeper. Specifics for the firing point, burn point, and impact point sampling follow.

The 60-mm firing point samples were conducted on fresh snow with no snow accumulation during the firing exercise. Three multi-increment surface samples using the 15-cm scoop were taken within the plume, followed by triplicate sub-surface samples taken with a 10-cm scoop from beneath the same area sampled with the 15-cm scoop. One multi-increment surface sample using the 10-cm scoop also was taken. Triplicate multi-increment OTP samples were taken between 0 to 3 m and 3 to 6 m from the plume's edge. Downrange from the firing position, triplicate multi-increment samples were taken from the four 3- $\times$ 10-m decision units established at 15 m, 25 m, 35 m, and 50 m from the FP (Fig. 2-7a).



a. 60-mm mortar firing.

**Figure 2-7. Firing position maps showing decision units sampled.**



**b. 81-mm mortar.**

**Figure 2-7 (cont'd). Firing position maps showing decision units sampled.**

The 81-mm firing point samples were taken while snow was falling so the methodology had to be modified to collect samples at a sufficient depth to capture most of the residues. Because of the accumulation of snow during the firing, the triplicate plume samples were sampled to a greater depth ( $\approx 6$  cm) with a 15-  $\times$  15-cm scoop, followed by deeper sampling ( $\approx 5$  cm) with the 10-cm square scoop (Fig. 2-8). Triplicate OTP multi-increment samples at 0 to 3 m and 3 to 6 m were taken. The downrange 3-  $\times$  10-m areas also were sampled in triplicate for this test as outlined above (Fig. 2-7b).

Following the 81-mm plume sampling, the burn points were created. One of the two burn points for each type of propellant was sampled. The small area of most intense residue ( $0.06$  to  $0.5$   $m^2$ ) as well as the OTP area out to about 0.5 m was completely sampled. Sampling was done with the 10-cm scoops. One set of burn points was left to be sampled at a later date. All burn points were recorded with a GPS unit.

The final samples collected were for the 60-mm impacts. Prior to post-detonation sampling, the plumes were inspected for continuity and overlap. The plumes, with the exception of the double plume, had clear visual separation between them, giving a preliminary indication of no cross contamination between detonations. They were visually demarcated and physically delineated by walking along the edge. The criterion used was a thinning of the plume to the point of difficulty in discerning continuous discoloration of the snow surface. The position and area were then recorded using a global positioning system.



**Figure 2-8. Collecting samples at 81-mm firing position.**

We collected approximately one hundred 0.01-m<sup>2</sup> increments from the entire plume for each sample. A single individual collected the triplicate samples from four of the plumes, three individuals each collected a multi-increment sample from one plume, and two individuals collected triplicate multi-increment samples from the double plume (Fig. 2-9). The logic for this plume sampling strategy was to test for the influence of individual samplers on residue recoveries.



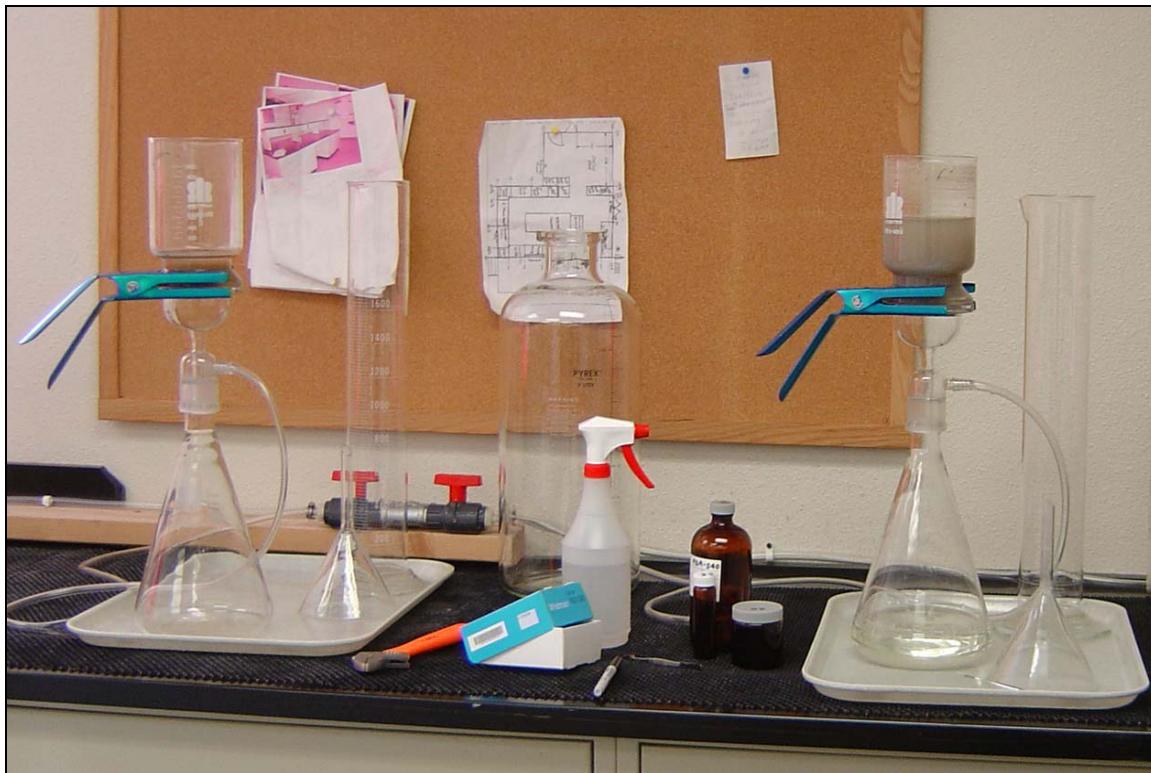
**Figure 2-9. Sampling double-impact plume.**

The dwindling daylight prevented us from conducting as much QA sampling as originally planned. Only one plume had subsurface samples taken beneath surface-sampled locations, and only one had triplicate OTP 0- to 3-m samples taken. The remainder of the plumes had a single 0- to 3-m OTP sample taken. No 3- to 6-m OTP samples were obtained. The final GPS work was done by vehicle headlights as the last rays of the setting sun faded.

### *Sample Processing and Analysis*

The multi-increment snow samples were transferred to a lab set up in the Fort Richardson cantonment area for processing. Upon arrival, the samples were transferred from the field bags to clean bags, double-bagged, and placed in clean polyethylene tubs for thawing. Placing the samples in clean bags reduces the chances of cross-contamination from contact with adjoining bags and residues on the exterior of the sample bags. Double-bagging and the tubs were necessary because of the inclusion of sharp pieces of the projectile (frag) or other debris collected with the snow samples. Frag inclusions or plant stems can pierce the sample bags, allowing the thawed sample to leak.

Samples were shifted from warmer to cooler areas of the logistics bay of the lab to prevent over-warming ( $>10^{\circ}\text{C}$ ) of the samples after melting. The samples were then processed based on completion of melting and sampled area. Samples anticipated to have the least residues were processed first and those anticipated to be more contaminated were done last. Again, this is to reduce the chances of any cross-contamination. Processing involves filtering the melted samples using a vacuum system and separating the soot fraction from the aqueous fraction (Fig. 2-10). The soot fraction is collected on filter papers (Whatman glass microfiber 90-mm  $\varnothing$  grade GF/A) and the filters are placed in a clean amber jar, dried, and stored in a refrigerator at  $<5^{\circ}\text{C}$ . A 500-mL aliquot of the filtrate was preconcentrated by passing it through a Waters Porapak RDX (Sep-Pak, 6-cm<sup>3</sup>, 500-mg) solid-phase extraction (SPE) cartridge and eluted with 5 mL of acetonitrile, resulting in a 100:1 concentration of the analytes (Walsh and Ranney 1998). The concentrate is split into two aliquots, 3.5 mL for analysis and 1.5 mL for archiving. When processing was completed, the 3.5-mL splits and the filters were shipped to the analytical chemistry laboratory at CRREL's main office in Hanover, New Hampshire, for final processing and analysis.



**Figure 2-10. Sample filtration setup.**

The filters containing the soot fractions were extracted using acetonitrile. Each sample was shaken with the solvent for 18 hours. The acetonitrile extracts from the solid-phase extraction of the melted snow and of the solid residue on the filters were analyzed by either HPLC or GC- $\mu$ ECD, depending on analyte concentration.

Analyte concentrations greater than 100  $\mu\text{g/L}$  were determined following the general procedures of SW 846 Method 8330 (Nitroaromatics and Nitramines by High-Performance Liquid Chromatography [HPLC]) (U.S. Environmental Protection Agency [USEPA] 1994). Lower concentrations were determined using Method 8095 (Nitroaromatics and Nitramines by GC) (USEPA 2000), which uses an electron capture detector and provides detection limits near 1  $\mu\text{g/L}$  for RDX and 20  $\mu\text{g/L}$  for NG in solvent extracts. The advantage of the HPLC method is that the analytical error is very small, about 2% relative standard deviation (RSD) for replicate injections. Although the GC- $\mu$ ECD method can detect much lower concentrations, the analytical error is much greater, approaching 20% RSD.

Prior to HPLC analysis, 1.00 mL of each acetonitrile extract was mixed with 3.00 mL of reagent-grade water. Determinations were made on a modular system from Thermo Electron Corporation composed of a Finnigan SpectraSYSTEM Model P4000 pump, a Finnigan SpectraSYSTEM UV2000 dual wavelength UV/VIS absorbance detector set at 210 and 254 nm (cell path 1 cm), and a Finnigan SpectraSYSTEM AS300 autosampler. Samples were introduced with a 100- $\mu$ L sample loop. Separations were achieved on a 15-cm  $\times$  3.9-mm (4- $\mu$ m) NovaPak C8 column (Waters Chromatography Division, Milford, Massachusetts) at 28°C and eluted with 1.4 mL/min of 15:85 isopropanol/water (v/v).

For GC analysis, the acetonitrile extracts were transferred to autosampler vials, which were then placed into an HP 7683 Series autosampler tray that was continuously refrigerated by circulating 0°C glycol/water through the trays. A 1- $\mu$ L aliquot of each extract was directly injected into the HP 6890 purged packed inlet port (250°C) containing a deactivated Restek Uniliner. Primary separation was conducted on a 6-m-  $\times$  0.53-mm-ID fused-silica column, with a 0.5- $\mu$ m film thickness of 5% (phenyl) methylsiloxane (RTX-5 from Restek). The GC oven was temperature-programmed as follows: 100°C for 2 min, 10°C/min ramp to 250°C. The carrier gas was hydrogen at 0.85 psi inlet pressure. The  $\mu$ ECD detector temperature was 280°C; the makeup gas was nitrogen at 60 mL/min. Extracts also were analyzed using an RTX-TNT2 confirmation column. Column dimensions were 6 m  $\times$  0.53 mm ID with a 1.5- $\mu$ m film thickness. The GC oven was temperature-programmed as follows: 130°C for 1 min, 10°C/min ramp to 160°C, 30°C/min ramp to 270. The carrier gas was hydrogen at 1.6 psi inlet pressure. The  $\mu$ ECD temperature was 310°C and the makeup gas was nitrogen at 60 mL/min.

All of the 81-mm mortar firing point samples and burn point samples were analyzed by HPLC. The 60-mm firing point samples were analyzed by both HPLC and GC. The 60-mm impact samples were analyzed by GC.

Calibration standards were prepared from analytical reference materials obtained from Restek Corporation (Bellefonte, Pennsylvania). The analytical reference materials were 8095 Calibration Mix A (1 mg/mL) and a single-component solution of NG (1 mg/mL). A spike solution at 1000  $\mu$ g/L was prepared from 8330 Calibration Mix 1 and the single-component solution of NG (1 mg/mL). Spiked water samples at 2  $\mu$ g/L were prepared by mixing 1.00 mL of the spike solution with 499 mL of water. Following SPE, the extract target concentration was 200  $\mu$ g/L for each analyte.

To calculate the mass of unreacted energetics deposited on the snow, we combined the estimated masses derived for the soot and aqueous fractions. For the aqueous fraction, we divided the average concentration of the extract ( $\mu$ g/L)

by 100. We then multiplied by the total volume of filtrate for the sample (L), giving us the mass dissolved in the snow ( $\mu\text{g}$ ). For the soot fraction, we multiplied the filter extract ( $\mu\text{g}/\text{L}$ ) by the volume of AcN used in the extraction process (L), giving us the mass of residues on the filter ( $\mu\text{g}$ ). We then combined these mass values and divided by the area sampled, giving us a mass-per-unit-area estimate ( $\mu\text{g}/\text{m}^2$ ). Multiplying this value by the measured area of the plume ( $\text{m}^2$ ) gives us the final estimate for the residue mass for that sample ( $\mu\text{g}$ ) (Jenkins et al. 2002, Hewitt et al. 2003).

### **Quality Control Procedures**

Quality control (QC) procedures were conducted both in the field and in the lab. Field QC, noted previously, included replicate sampling within the residue plumes, sampling outside the demarcated plumes, using multiple sampling methods, and sampling below previously sampled points.

We also conducted QC procedures in the processing lab. Blank samples consisting of filtered water (Barnstead E-Pure filtration system:  $80 \text{ M}\Omega$  minimum) were periodically run through a filter assembly and SPE setup for later analysis at the lab. This procedure was designed to determine whether cross-contamination from the sample filtering apparatus was occurring. Water fractions for several samples were divided into three aliquots and run through the SPE to determine whether recovery rates from the SPE procedure were consistent. SPE blanks were run to determine cartridge filter retention and recovery during the elution process. These processes are described in greater detail in Walsh et al. (2005c).

## **Results**

### *Background Samples*

The background samples collected from the FP areas prior to firing were blank, indicating clean test areas. Results are given in Table 2-3.

### *Firing Points*

A total of 49 multi-increment samples, composed of 2,676 increments, were taken. The demarcated plume sizes were  $158 \text{ m}^2$  for the 60-mm FP and  $135 \text{ m}^2$  for the 81-mm FP. Because of the difficulty of demarcating the 81-mm FP plume and based on the analysis of the OTP samples, the FP plume analysis was done for both the original demarcated plume area and an expanded plume that includes

the OTP area ( $365 \text{ m}^2$ ). Sampling and plume data are given in Table 2-2. Maps of the test areas derived from the GPS data are shown in Figure 2-7.

**Table 2-2. Data for sampled areas: Firing positions.**

<b>Position</b>	<b>Decision unit</b>	<b>Sampling tool size (cm)</b>	<b>Decision unit size (<math>\text{m}^2</math>)</b>	<b>Average area sampled (<math>\text{m}^2</math>)</b>	<b>Average area sampled (%)</b>
60 mm	Plume: Surface	$15 \times 15 \times 2$	158	0.89	0.56%
	Plume: Surface*	$10 \times 10 \times 2$	158	0.77	0.63%
	Plume: Subsurface	$10 \times 10 \times 2$	158	0.40	0.25%
	OTP: 0–3 m	$10 \times 10 \times 2$	168	0.75	0.45%
	OTP: 3–6 m	$10 \times 10 \times 2$	220	0.72	0.33%
	15-m transect	$10 \times 10 \times 2$	77	0.60	0.78%
	25-m transect	$10 \times 10 \times 2$	101	0.60	0.59%
	35-m transect	$10 \times 10 \times 2$	70	0.50	0.71%
	50-m transect	$10 \times 10 \times 2$	101	0.52	0.51%
81 mm	Plume: Surface	$15 \times 15 \times 2$	135	0.96	0.71%
	Plume: Subsurface	$10 \times 10 \times 2$	135	0.43	0.32%
	OTP: 0–3 m	$10 \times 10 \times 2$	155	0.60	0.39%
	OTP: 3–6 m	$10 \times 10 \times 2$	210	0.51	0.24%
	15-m transect	$10 \times 10 \times 2$	50	0.60	1.2%
	25-m transect	$10 \times 10 \times 2$	71	0.60	0.85%
	35-m transect	$10 \times 10 \times 2$	84	0.50	0.60%
	50-m transect	$10 \times 10 \times 2$	61	0.53	0.87%
	Note: N = 3 for all samples except *(N = 1).				

Analytical data averaged for the replicates are given in Table 2-3. Two significant digits are used for the data in this table and throughout this report. The samples were analyzed for a series of energetic compounds: TNT, TNB, 1,3-DNB, 2,4-DNT, RDX, HMX, and NG. Only NG was detected in any of the firing point samples.

The plume in front of the 60-mm FP contained only low concentrations of NG. The OTP and downrange transects contained no detectable quantities of NG, indicating that the demarcated plume held the majority of residues. Subsurface samples also had no detectable quantities of NG, indicating that the surface samples were of adequate depth. Detected mass for the plume averaged 2.7 mg for the triplicate samples ( $\approx 40$  increments each) and was 0.8 mg for the single 10-cm multi-increment sample (77 increments). Including this sample with the triplicates gives an average mass of 2.2 mg. A total of 25 samples comprising 1,420 increments was taken at the FP.

**Table 2-3. Analytical data for NG in plumes: Firing point tests.**

<b>Position</b>	<b>Sample type*</b>	<b>Replicate mass (mg)</b>	<b>Average mass (mg)</b>	<b>Range ratio</b>
Both	Background	—	ND	—
60 mm	Plume: 15- × 15-cm scoop	4.9		
		1.3		
		2.0	2.7	3.7
	Plume	0.76	2.2 <sup>†</sup>	6.4 <sup>†</sup>
	Plume: Subsurface	ND	—	—
	OTP: 0–3 m	ND	—	—
	OTP: 3–6 m	ND	—	—
	15-m transect	ND	—	—
	25-m transect	ND	—	—
	35-m transect	ND	—	—
	50-m transect	ND	—	—
81 mm	Plume: 15- × 15-cm scoop	58,000		
		41,000		
		53,000	51,000	1.4
	Plume: Subsurface	17,000		
		14,000		
		8,500	13,000	2.0
	OTP: 0–3 m	150		
		210		
		570	310	3.8
	OTP: 3–6 m	60		
		83		
		96	80	1.6
	15-m transect	12		
		15		
		20	16	1.7
	25-m transect	41		
		2.1		
		2.8	15	19
	35-m transect	5.5		
		4.0		
		5.5	5.0	1.4
	50-m transect	1.2		
		1.5		
		1.8	1.5	1.5
	Plumes + Subsurface		64,000	—
	Plumes + Subsurface + OTPs		64,000	—

ND = Not detected by analytical instrumentation

\* Sample taken with 10- × 10-cm scoop unless otherwise noted

† Average of all four multi-increment samples

The 81-mm FP was quite different from the 60-mm position. Both the surface and subsurface samples for the demarcated plume had gram-quantities of NG. The subsurface residues are indicative of the deposition of residues throughout the snowstorm the night of 18 January. Both the OTP triplicate samples also contain NG residues, albeit at a much reduced mass. The down-range transects all contain measurable quantities of NG. Repeatability for all samples is within a factor of two except for the 25-m transect, which appears to have contained a partial propellant grain (likely due to the proximity of the second 81-mm mortar FP) and one of the OTP samples. For characterization purposes, we lumped the subsurface measurements with the surface measurements and looked at the effect of adding the OTPs with the plume, giving us a new plume size of 500 m<sup>2</sup> with the OTPs. The adjusted total residue (to two significant digits) is affected by the subsurface samples (20% of combined total) but not by the OTPs (<0.3%). Although the OTP residues are significant by themselves, they are not significant when taken in context with the original plume NG residue mass load. A total of 24 samples comprising 1,300 increments was taken at the FP. A more complete data set can be found in Appendix B.

Extrapolating further, we expanded the 81-mm firing point plume out to the 50-m transect, enlarging the plume area to encompass all the sampled decision units as well as the areas in between (Fig. 2-11). The objective of this exercise was to test whether expanding the plume downrange will significantly increase the estimated mass of residues. The new plume was divided into areas based on the location of the sampled transects. The residue mass within each transect was then calculated using mass concentration data derived from Tables 2-2 and 2-3.

$$\text{Recalculated mass } (\mu\text{g}) = \text{Transect mass concentration } (\mu\text{g/m}^2) * \\ \text{Transect zone area } (\text{m}^2). \quad (1)$$

The recalculated NG residue masses from these zones were added to the original mass calculation for the plume surface, subsurface, and OTP values. We did not try to correct for the influence of the second 81-mm mortar position in this analysis, which added to the residue load in part of the expanded plume. With the 60-mm firing position, there is of course no effect as no residues were detected outside the demarcated plume.

The theoretical plume that encompasses the original demarcated plume, the OTPs, and the transects has an estimated mass larger than the separate decision units combined. The increases in mass for the expanded transects (transect zones in Fig. 2-11) range from 138% to 420%. The projected mass difference is 98 mg (360% of original mass for all transects). Although significant within the context

of the area beyond the OTPs, the recalculated mass is not significantly greater than the original mass calculations (<0.2%). Data are given in Table 2-4.

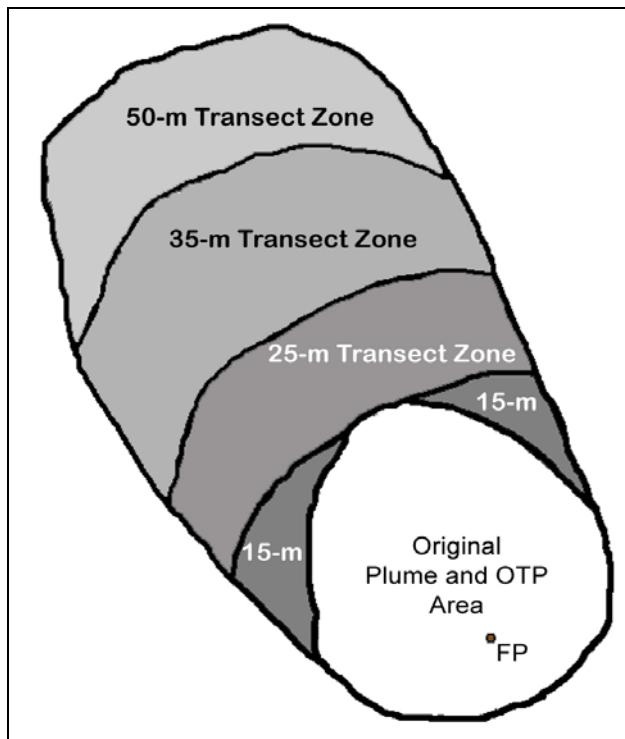


Figure 2-11. Extrapolated 81-mm FP plume using expanded transect zones.

**Table 2-4. Estimated FP residue mass values using plume extrapolation: 81-mm mortar.**

Decision unit	Decision unit size: New (m <sup>2</sup> )	Original mass (mg)*	Recalculated mass (mg)	Difference from original (%)
Plume	135	64,000	64,000	—
OTP: 0–3 m	168	310	310	—
OTP: 3–6 m	210	80	80	—
15-m transect zone	120	16	38	138%
25-m transect zone	295	15	64	327%
35-m transect zone	433	5.0	26	420%
50-m transect zone	320	1.5	7.7	413%
Transect mass		38	136	360%
Theoretical plume	1680	64,428	64,526	0.15%

\* From Table 2-3

A rough mass balance can be done on the NG load in the propellants (Table 2-1). Table 2-5 contains data on the number and types of rounds fired from the two test positions as well as the sources of and the total masses of NG involved. Using these data as well as those from Tables 2-3 and 2-4, the results in Table 2-6 were derived.

The analysis for the 60-mm mortar is straightforward, as only one type of round was fired from the mortar position. The only propellant component with NG was the ignition cartridge. For the 81-mm mortar, two types of rounds with differing propellant charges were used. The M301A3 illumination round has NG in both the propelling charges and the ignition cartridge, whereas the M374A3 HE round has NG only in the ignition cartridge. This makes deriving the per-round mass balance difficult. What we did in Table 2-6 was estimate the ignition cartridge efficiency for the 81-mm rounds as equivalent to the 60-mm round. That gives us a value for the 81-mm HE ignition cartridges, from which we can derive an estimate for the M374A3 round. Using this value, we calculated a value for the M301A3 round. Further analysis of the M301A3 round will yield a rough estimate of the mass balance for the propelling charges, but the utility of such an estimate is questionable. Previous work (Jenkins et al. 2000b) indicates that NG from the ignition cartridge also can be found at the detonation point of mortar rounds, although we did not find any in our samples.

**Table 2-5. Original masses of NG utilized in firing point tests.**

Position	Type of round	Source of NG	Sources consumed	Mass of NG in source (g)	Total mass (g)
60 mm	M888	Primer	25	0	0
		Ignition	25	1.35	33.8
		M204 charge	5	0	0
Total					33.8
81 mm	M301A3	Primer	61	0	0
		Ignition	61	2.98	181.8
		M185 charge	314	5.31	1,667.3
	M374A3	Primer	40	0	0
		Ignition	40	2.98	119.2
		M205 charge	81	0	0
Total					1,968.3

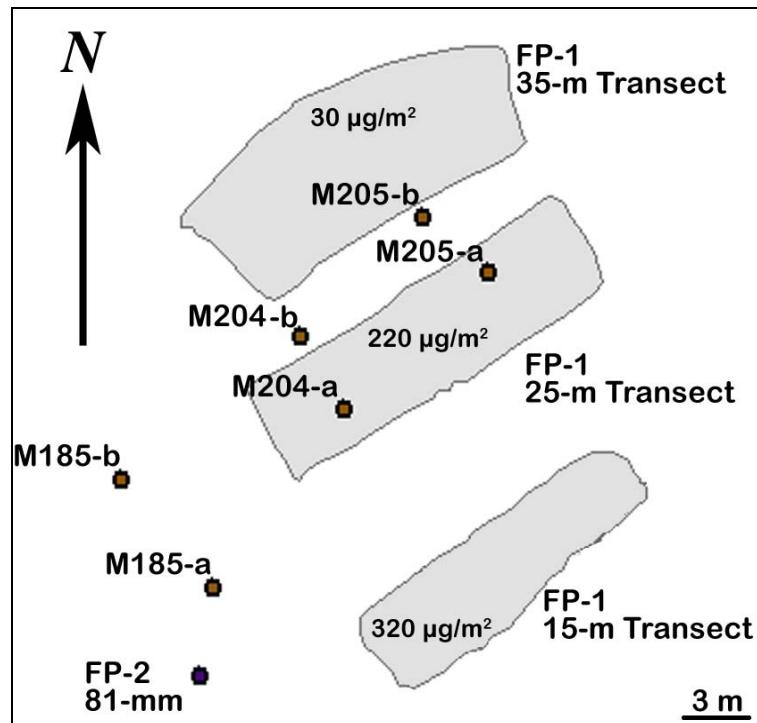
**Table 2-6. Calculated mass balance for NG in propellants for mortar cartridges.**

Position	Type of round	Original mass (g)	Recovered mass (g)	Number of rounds	Recovered mass (%)	Mass per round (mg)
60 mm	M888	33.8	0.0022	25	$6.5 \times 10^{-3}$	0.088
81 mm	M301A3	1849	64	61	3.5%	1000
	M374A3	119	0.0077*	40	$6.5 \times 10^{-3}$	19

\* The estimate for the M374A3 round was derived from the M888 round.

### Burn Points

Propellant charges for each of the three different mortar cartridges were burned in two piles of ten each. These piles were on the snow surface and unconfined (Fig. 2-6). No specific background samples were taken at these locations. We relied instead on data collected from the transect samples taken for the just-completed 81-mm FP test. Those samples indicated NG levels ranging from  $320 \mu\text{g}/\text{m}^2$  to  $60 \mu\text{g}/\text{m}^2$  as the distance from the firing position (FP-1) increased. Figure 2-12 is a map of the burn points. Appendix C contains more complete data for this test.

**Figure 2-12. Burn point map.**

One of the two burned piles (-a) was sampled for each propellant type. Because these areas were not large, they were sampled completely (Table 2-7). An area surrounding the burn area also was sampled. A total of one multi-increment and five discrete samples was taken at the burn points. The second burn area (-b) was left for sampling in the future to determine whether any attenuation of the energetic residues occurs over the winter.

**Table 2-7. Data for sampled areas: Burn points.**

Charge/propellant	Decision unit	Decision unit size (m <sup>2</sup> )	Area sampled (m <sup>2</sup> )	Area sampled (%)
M185/M9	Burn point (a)	0.063	0.063	100%
	OTP	0.50	0.50	100%
M204/M10	Burn point (a)	0.44	0.44	100%
	OTP	0.34	0.34	100%
M205/M10	Burn point (a)	0.54	0.54	100%
	OTP	0.46	0.40	87%

The samples were analyzed for a series of energetic compounds: TNT, TNB, 1,3-DNB, 2,4-DNT, RDX, HMX, and NG. During the melting and filtering process, it was visually evident by color that a large amount of material was present in the aqueous portion (Fig. 2-13). Thinking this was indicative of high quantities of unreacted residues, we processed these samples last and tried to keep the pre- and post-processed samples separated from other samples to prevent cross contamination.

The data for the burn point sample analyses are presented in Table 2-8. Only NG was detected in any of the samples. From Table 2-1, only the M185 charge contains NG. Analysis of the data indicates that about 1.7% of the original NG in the propellant remains after unconfined burning. The analyses of the M204 and M205 samples indicate trace amounts of NG in the OTP samples but none detected in the burn point samples. This is likely an artifact from the previous firing of the rounds from the mortar positions. The detection levels in the OTPs are consistent with the 30- to 220- $\mu\text{g}/\text{m}^2$  levels in the 25- and 35-m transects that are used as background levels for this test (Fig. 2-12). For the M204 OTP, the background level should be around 0.097 mg for the area sampled. For the M205 OTP, the background level should be closer to 0.012 mg for the area sampled. Both data points are close to these values, indicating that the NG recovered was from the background residues resulting from the firing of the 81-mm mortars. These quantities are small compared to the residues recovered for M185 propellant burn.



**Figure 2-13. Filtering propellant burn area sample (M205-a).**

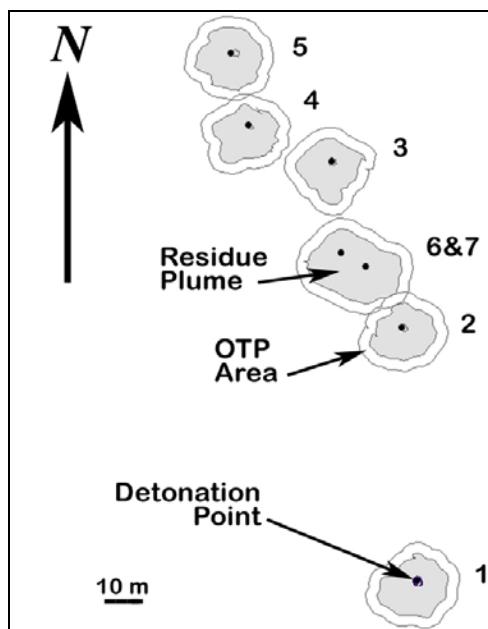
**Table 2-8. Analytical data for NG in plumes: Burn point tests.**

Propellant	Decision unit	Original mass (mg)	Recovered mass (mg)	Mass remaining
M185	Burn point (a)	53,100	840	1.6%
	OTP	0.0	33	0.06%
M204	Burn point (a)	0.0	-ND-	—
	OTP	0.0	0.071	—
M205	Burn point (a)	0.0	-ND-	—
	OTP	0.0	0.023	—

#### *Impact Points*

Seven M888 mortar round impacts were sampled. Of the seven, five generated non-overlapping plumes and two detonations overlapped, creating a double-impact plume. The rounds were fired on a cold ( $-13^{\circ}\text{C}$ ) windless day during a light snowfall. The plumes were generally concentric around the detonation points (Fig. 2-14). Samples were taken both within the demarcated plumes and within a 0- to 3-m annulus surrounding the plumes. A total of 34 multi-increment samples consisting of 2,732 increments was collected. Table 2-9 contains the physical data for the plumes. Appendix D contains more detailed data for this test.

Each M888 cartridge body contains 358 g of Comp B high explosive consisting of 215 g of RDX and 140 g of TNT. Up to 9% of the RDX (19 g) can be HMX, a manufacturing by-product of RDX. The M935 point-detonating fuze contains an additional 15 g of RDX. Detonation residues were analyzed for TNT, TNB, 1,3-DNB, 2,4-DNT, RDX, HMX, and NG. Only RDX was detected in the samples. Table 2-10 contains the analytical data for the analyses of the impact area samples.



**Figure 2-14. 60-mm M888 HE round detonation plumes: Sampled plumes.**

The average residue mass deposition was 73 µg RDX per detonation, ranging from a high of 190 µg to a low of 43 µg with a median of 50 µg, based on the residues of plumes 6 and 7 being evenly split between the two detonations. The repeatability between replicates is very good, averaging less than a factor of two difference between the high and low values (range ratio). Only one set of replicates has a difference greater than a factor of two, plume #1 at 2.3. The relative standard deviation (RSD) for the samples ranges from 16% to 39%. If we pool all of the percent RSD estimates, we obtain an overall estimate of 26% with 15 degrees of freedom. There were no explosives detected outside the demarcated plumes, and the one plume that was sampled beneath surface sample points had no detectable explosives in the subsurface samples. These QA results indicate a good representation of the residues from the detonations.

**Table 2-9. Data for sampled areas: Impact points.**

<b>Plume</b>	<b>Decision unit</b>	<b>Sampling scoop size (cm)</b>	<b># of samples</b>	<b>Decision unit size (m<sup>2</sup>)</b>	<b>Average area sampled (m<sup>2</sup>)</b>	<b>Average area sampled (%)</b>
1	Plume: Surface	10	3	233	0.91	0.39%
	OTP: 0–3 m	10	3	200	0.96	0.48%
2	Plume: Surface	15	3	200	1.0	0.50%
	Plume: Subsurface	10	3	200	0.42	0.21%
	OTP: 0–3 m	10	1	186	0.49	0.26%
3	Plume: Surface	10	3	207	1.0	0.48%
	OTP: 0–3 m	10	1	194	0.53	0.27%
4	Plume: Surface	10	3	201	0.92	0.46%
	OTP: 0–3 m	10	1	192	0.56	0.29%
5	Plume: Surface	10	3	228	0.99	0.44%
	OTP: 0–3 m	10	1	194	0.60	0.31%
6 & 7	Plume: Surface	10	6	360	1.0	0.28%
	OTP: 0–3 m	10	3	238	0.72	0.30%
Average	Plumes	—	3.5	214*	0.97	0.41%
	OTPs	—	1.7	193*	0.64	0.31%
Median	Plumes	—	—	207*	0.99	0.44%
	OTPs	—	—	194*	0.60	0.29%

\* Does not include the double plume (6 & 7)

**Table 2-10. Analytical data for RDX in plumes: Impact point test.**

Plume	Sample type	Replicate mass (µg)	Average mass (µg)	Range ratio	% RSD
1	Plume: LIS	51			
	Plume: LIS	100			
	Plume: LIS	120	90	2.3	39
	OTP: 0–3 m	ND			
	OTP: 0–3 m	ND			
	OTP: 0–3 m	ND	—	—	
2	Plume: LIS	47			
	Plume: LIS	60			
	Plume: LIS	36	48	1.7	25
	Plume: Subsurface	ND			
	Plume: Subsurface	ND			
	Plume: Subsurface	ND	—	—	
3	OTP: 0–3 m	ND	—	—	
	Plume: LIS	200			
	Plume: LIS	160			
	Plume: LIS	220	190	1.4	16
4	OTP: 0–3 m	ND	—	—	
	Plume: LIS	31			
	Plume: LIS	58			
	Plume: LIS	40	43	1.9	32
5	OTP: 0–3 m	ND	—	—	
	Plume: LIS	81			
	Plume: LIS	54			
	Plume: LIS	46	60	1.8	30
6 & 7	OTP: 0–3 m	ND	—	—	
	Plume: LIS	67			
	Plume: LIS	100			
	Plume: LIS	100			
	Plume: LIS	110			
	Plume: LIS	120			
	Plume: LIS	120	100	1.8	19
	OTP: 0–3 m	ND			
Average	OTP: 0–3 m	ND			
	Plumes (N = 6)		88	1.8	
Range	Detonations (N = 7)		73	1.7	
	Plumes		147	0.9	
Median	Detonations		147	1.2	
	Plumes		90	1.8	
	Detonations		50	1.7	

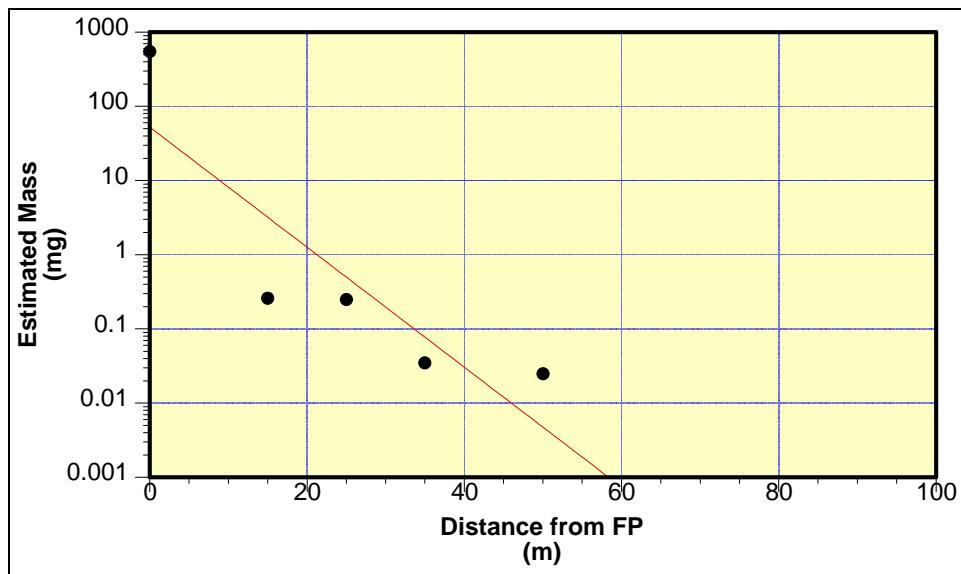
## Discussion

Testing out of doors always presents challenges. In our case, snow was the confounding factor. At the time of the tests, it was falling quite heavily for a period (Fig. 2-5 and 2-7), making plume demarcation especially difficult at the 81-mm firing point. We compensated for this to some extent by sampling deeper, 6 cm or more instead of the usual 2 cm. In this case, the subsurface samples were critical, amounting to 25% of the surface residue load or 20% of the total residue load within the plume. We were quite concerned that we had not adequately delineated the plume, and the results somewhat bear this out, with an estimated total of 390 mg of NG recovered from the 6-m-wide annulus surrounding the plume. However, when taken into context with the recovered residue load from within the plume (64 g), the quantity is not very significant ( $\approx 0.6\%$ ). Almost 80% of this was within the first 3 m of the annulus, indicating that we were a little undersized on the plume delineation but not enough to significantly affect the results.

The downrange firing point transects were of great interest. We did not have a good feel for the distance over which detectable amounts of residues could be found at a firing point. Previous work (Pennington et al. 2002, Walsh et al. 2004, Ramsey et al. in press) has been done at firing points but the ability to determine residues on a per-round basis was not possible. We have come closer in this study. The M185 propellant charges were the only charges containing NG, the only energetic constituent recovered from the 81-mm transects. Although NG is found in the ignition cartridges as well, the quantity is low and, from the 60-mm mortar test results, very little NG from the cartridges is deposited at the firing points after firing. If we assume that the contribution from the M374A3 ignition cartridges is minimal and that all the NG found in the transects is from the propellant charges of the 61 M301A3 cartridges fired, we get the following estimate for mass per round at each of the transects: 15 m: 260  $\mu\text{g}/\text{round}$ ; 25 m: 250  $\mu\text{g}/\text{round}$ ; 35 m: 82  $\mu\text{g}/\text{round}$ ; and 50 m: 25  $\mu\text{g}/\text{round}$ . This compares to the 1.1 g/round found within the combined plume/OTP area. We could not go out more than 50 m for this test as we would have been over the edge of a bluff and into the woods. Using exponential curve fitting,

$$Y = 52.595 * e^{-0.186X} \quad (2)$$

and assuming the mass at  $X = 0.0$  is equal to half the plume load (500 mg), we get a value of 1  $\mu\text{g}/\text{round}$  at  $\approx 60$  m out from the firing point ( $R^2 = 0.997$ ) (Fig. 2-15).

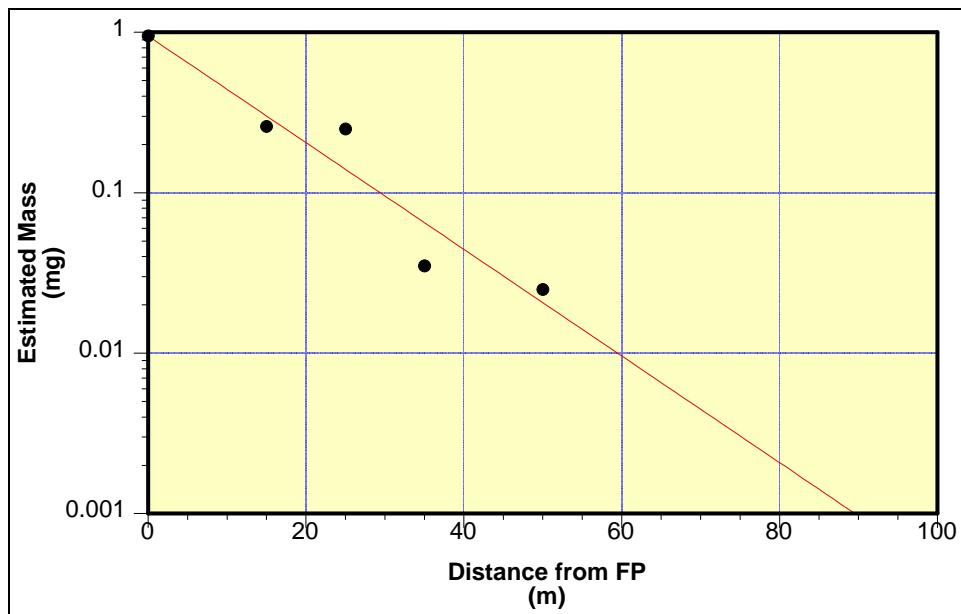


**Figure 2-15. Exponential curve fit for FP residues (●): Case 1.**

Curve fitting for only the transects, we get

$$Y = 0.9494 * e^{-0.0765X} \quad (3)$$

which gives us a value of 1 µg/round NG at 90 m ( $R^2 = 0.988$ ) (Fig. 2-16). The actual cutoff for 1 µg/round is likely between the distances given by (2) and (3).



**Figure 2-16. Exponential curve fit for FP residues (●): Case 2.**

We had similar concerns with the impact point samples. The snow was tapering off when the troops fired the rounds and the plumes were easier to delineate. Still, a thin covering of snow overlaid the detonation plumes. We were running up against sunset when we started sampling, so we had time to do only the 0- to 3-m OTP samples on the plumes. In this case, the OTP samples had no detectable residues, indicating that the plume delineations were sufficient. The one plume from which triplicate subsurface samples were taken also had no detectable energetics.

In our ongoing effort to examine the possible sources of error in our field sampling method, we conducted some tests while sampling the impact plumes. In one test, three samplers each obtained a multi-increment sample from within and outside a detonation plume. The data were compared for variability. The samplers were then randomly assigned a plume from which they were to obtain triplicate samples to test how repeatable their sampling was in comparison to the jointly sampled plume. Data are shown in Table 2-11.

**Table 2-11. Sampler variation test results.**

Sampler	Sample type	Replicate mass ( $\mu\text{g}$ )	Average mass ( $\mu\text{g}$ )	Range ratio
1	Plume: Impact #1	51		
2	Plume: Impact #1	100		
3	Plume: Impact #1	120	90	2.3
1	Plume: Impact #5	81		
	Plume: Impact #5	54		
	Plume: Impact #5	46	60	1.8
2	Plume: Impact #3	200		
	Plume: Impact #3	160		
	Plume: Impact #3	220	190	1.4
3	Plume: Impact #4	31		
	Plume: Impact #4	58		
	Plume: Impact #4	40	43	1.9
4	Plume: Impact #6 & 7	67		
	Plume: Impact #6 & 7	100		
	Plume: Impact #6 & 7	100	89	1.5
5	Plume: Impact #6 & 7	110		
	Plume: Impact #6 & 7	120		
	Plume: Impact #6 & 7	120	120	1.1

What is indicated in our limited study is that different samplers may recover different quantities of energetic residues from a plume but the difference may not be significant. Comparing the results of impact plume #1 with those of impact plumes #3–5, the spread of values for plume #1 (2.3x) is larger than for the triplicate samples done by each sampler (average difference of 1.7x), but both are around 2. A range for replicates in this type of test of two or less is considered very good. For the double plume, two samplers each took triplicate samples to get a better grasp of the difference between individuals. In this case, one individual averaged a recovery of 89 µg of RDX with a spread of 1.5x whereas the other sampler averaged a recovery of 120 µg with a spread of 1.1x. The spread between the two samplers is 1.3x, with no overlap between the replicate groups. Five of the six replicates are within 20%, a very close match. This indicates a small but consistent difference.

Two other factors pertaining to the nature of the material being sampled should be noted. The residues for the impact point plumes and areas outside the firing points had very low concentrations of residues. Many times, the analysis indicates that the concentrations of the sample residues are at or near the detection limits of the analytical instrumentation. This normally makes analyses for these decision units difficult, as a very small amount of residues can make a large relative difference between replicates. We were fortunate for the most part not to have this problem. In two cases, we had what are often called outliers, or abnormally high residue values (81 FP OTP 0–3 and 81 FP 25-m transect). When firing mortars, pieces of the propellant container are ejected along with the projectile. This debris may be indicative of unburned propellant. The heterogeneous nature of this distribution and the increased distance the particles may be thrown makes consistent sampling difficult and may have led to the high values at these two decision units.

It is interesting to note the differences between the burn points, firing points, and impact points. For the burn points, we recovered about 2% of the original mass of NG in the propellant of the M185 charge after burning. At the firing point, the recovery was about 3%. These values are very close. For the impact points, the recovery rate averaged a mere  $2 \times 10^{-5}\%$ . There is a tremendous difference in residue deposition between high-order detonations and firing points. This is further emphasized by the small area over which the FP deposition may occur (150 m<sup>2</sup> in our tests) and the large area the impact plumes encompass (over 1,400 m<sup>2</sup> for the six rather small 60-mm plumes sampled). There is a difference in the original mass of energetics, 2 kg of NG for 100 rounds vs. 2.6 kg of HE for seven rounds, but the concentration of residues at firing points can quickly accrue. This is not to say that the explosive load of the projectiles isn't a concern. Two of the 10 rounds fired during our test did not detonate, depositing 730 g of

HE on the Flats. When the bodies of these projectiles eventually corrode and the explosive load leaches out onto the firing range, a high-level point source will occur (Taylor et al. 2004). If 1,000 M888 rounds are fired into an impact area and the dud rate is 20%, as we witnessed during our study, over 73 kg of HE (60% RDX, 39% TNT) will be distributed within a limited area of the impact area and will eventually be released into the environment. With the millions of rounds fired each year in training ranges throughout the United States and the world (Dauphin and Doyle 2000), the need for the accurate tracking of munitions to maintain viability of our training ranges is obvious.

This study was conducted in association with a training exercise by the Army. Although the troops were very cooperative and assisted whenever possible, their mission was training and not research support. We therefore did not have control over how the tests were conducted or when. Ideally, we would have had the mortars set up alone in a large field, firing a fixed number of rounds with a fixed number of propellant charges each. This would have given us a better understanding of the per-round propellant residues loading. In the future, this may happen. The information we did get from these tests is a great start and we thank the troops for the opportunity to work with them and also for their efforts beyond the call of duty to help us with this critical research.

## Conclusions

A series of firing point tests were conducted on energetics associated with a live-fire training mission involving 60-mm and 81-mm mortars at Fort Richardson, Alaska, in January 2006. A firing point was sampled for the 60-mm M19 mortar firing 25 M888 HE cartridges with varying quantities of M204 propellant charges. Residues recovered from the demarcated plume ( $158\text{ m}^2$ ) indicated 0.65% of the original NG propellant load remained. No other constituents were detected (we did not analyze for nitrocellulose [NC], the major energetic constituent of the propellant) and no energetic residues were detected outside the demarcated plume. A firing point also was sampled for the 81-mm M252 mortar firing 40 M374A3 HE cartridges and 61 M301A3 illumination cartridges with varying quantities of M205 and M185 propellant charges, respectively. Residues collected from within the demarcated plume ( $135\text{ m}^2$ ) indicated that 3.3% of the original NG propellant load remained, mostly from the 61 M301A3 rounds (>98%). The M185 propellant charge contains NG, whereas the M205 charge does not. A significant amount of NG was recovered from samples taken from a  $380\text{-m}^2$  annulus around the demarcated plume, but this quantity amounted to only 0.61% of the recovered NG from within the plume. Smaller quantities of NG were detected out to the limits of our sampling (50 m) with a projected deposition

distance of between 60 and 90 m downrange for the conditions under which we tested.

A series of burn point tests were conducted following firing point tests. Unconfined 10-charge piles for each of the three different cartridges were burned on the snow surface, sampled, and analyzed. Only one of the three propellants, the M9 propellant in the M185 charge, had detectable quantities of energetics following burning. About 2% of the original NG load was recovered. Again, we did not analyze for NC.

Following the burn point tests, 10 M888 mortar rounds were fired into the Flats. Eight of the 10 rounds detonated, and seven of the eight detonation points comprising six plumes were sampled for energetic residues. Only RDX was recovered from the plumes. The average residue quantity per detonation was  $73 \mu\text{g}$ ,  $2 \times 10^{-5}\%$  of the original HE load. No detectable residues were found in subsurface or OTP samples. While collecting samples, we conducted tests on consistency among and repeatability for different samplers. In a limited study examining sampling repeatability among several samplers, we found that individual samplers are able to sample in a very repeatable manner (range  $<1.7x$ ), but there may be a significant difference in the range of recoveries between samplers. For single multi-increment samples the range between samplers was 2.3x and for triplicate multi-increment samples the range between samplers was 1.3x. Overall repeatability of triplicate samples was quite good for all replicates ( $N = 24$  sets of three) with only three sets with a range greater than 2.0x.

This study reinforces the importance of maintaining firing points to avoid their becoming a source of energetic residues on ranges. Burn points have not been addressed in a focused manner and may become the next area of research required for a holistic approach to munitions management and range sustainability. High-order detonations of munitions in impact areas are not a critical consideration in range sustainment, but tracking dudded rounds needs to have a higher priority than current practice as these rounds will become an energetics source in the future.

These results are estimates of unreacted residues from activities associated with a live-fire mortar mission. They are indicators of possible residue masses that will result from such activities. Many values are at or near detection limits for the analytical instrumentation and difficult to interpret. It is important to keep in mind that there is much variability between activities and some variability between rounds and that these results should be considered to be approximate.

## References

**Dauphin, L., and C. Doyle** (2000) Study of ammunition dud and low order detonation rates. U.S. Army Defense Ammunition Center–Technical Center for Explosives Safety. Technical report written for U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland.

**Hewitt, A.D., T.F. Jenkins, T.A. Ranney, J.A. Stark, M.E. Walsh, S. Taylor, M.R. Walsh, D.J. Lambert, N.M. Perron, N.H. Collins, and R. Kern** (2003) Estimates for explosives residues from the detonation of army munitions. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-03-16.

**Jenkins, T.J., T.A. Ranney, P.H. Miyares, N.H. Collins, and A.D. Hewitt** (2000a) Use of surface snow sampling to estimate the quantity of explosives residues resulting from land mine detonations. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-00-12.

**Jenkins, T.J., T.A. Ranney, M.E. Walsh, P.H. Miyares, A.D. Hewitt, and N.H. Collins** (2000b) Evaluating the use of snow-covered ranges to estimate the explosives residues that result from detonation of army munitions. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-00-15.

**Jenkins, T.F., M.E. Walsh, P.H. Miyares, A.D. Hewitt, N.H. Collins, and T.A. Ranney** (2002) Use of snow-covered ranges to estimate explosives residues from high-order detonations of army munitions. *Thermochimica Acta*, **384**: 173–185.

**Jenkins, T.F., A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, and K.L. Bjella** (2005) Representative sampling for energetic compounds at military training ranges. *Environmental Forensics*, **6**: 25–55.

**Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, D. Lambert, J. Clausen, and J.J. Delfino** (2002) Distribution and fate of energetics on DoD test and training ranges: Interim Report 2. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC TR-02-8.

**Ramsey, C.A., S. Taylor, and M.E. Walsh** (in prep) Propellant residues from the 105s.

**Taylor, S., J.H. Lever, B. Bostick, M.R. Walsh, M.E. Walsh, and B. Packer** (2004) Underground UXO: Are they a significant source of explosives in soil compared to low- and high-order detonations? U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, ERDC/CRREL Technical Report TR-04-23.

**U.S. Army** (1969) Military Standard: Propellants, solid, for cannons: Requirements and packing. MIL-STD-652C (MU) U.S. Government Printing Office, Washington, DC.

**U.S. Army** (1981) Military Specification: Propellant, M1 for 60-mm mortar M204 propelling charge. MIL-P-63194A (AR) U.S. Government Printing Office, Washington, DC.

**U.S. Army** (1982) Military Specification: Propellant, M1 for 81-mm mortar M205 propelling charge. MIL-P-48130A (AR) U.S. Government Printing Office, Washington, DC.

**U.S. Army** (1998) Propellant management guide. U.S. Army Defense Ammunition Center, Logistics Review and Technical Assistance Office, Savanna, Illinois.

**U.S. Environmental Protection Agency** (1994) SW846 Method 8330. Nitroaromatics and nitroamines by HPLC. USEPA Office of Solid Waste standard methods of analysis test methods for evaluating solid wastes, physical and chemical methods. Update II (<http://www.epa.gov/sw-846/pdfs/8330.pdf>).

**U.S. Environmental Protection Agency** (2000) SW846 Method 8095. Explosives by gas chromatography. Update IVB ([www.epa.gov/epaoswer/hazwaste/test/pdfs/8095.pdf](http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8095.pdf)).

**Walsh, M.E., and T.A. Ranney** (1998) Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and GC-ECD. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Special Report 98-2.

**Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney** (2001) Sampling for explosives residues at Fort Greely, Alaska. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, ERDC/CRREL Technical Report TR-01-15.

**Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T.S. Douglas, N. Perron, D. Lambert, R. Bailey, and K. Myers** (2004) Range characterization studies at Donnelly Training Area, Alaska: 2001 and 2002. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, Technical Report ERDC/CRREL TR-04-3.

**Walsh, M.R., M.E. Walsh, C.A. Ramsey, and T.F. Jenkins** (2005a) An examination of protocols for the collection of munitions-derived explosives residues on snow-covered ice. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, ERDC/CRREL Technical Report TR-05-08.

**Walsh, M.R., S. Taylor, M.E. Walsh, S.R. Bigl, K. Bjella, T.A. Douglas, A.B. Gelvin, D.J. Lambert, N.M. Perron, and S.P. Saari** (2005b) Residues from live-fire detonations of 155-mm howitzer rounds. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, ERDC/CRREL Technical Report TR-05-14.

**Walsh, M.R., M.E. Walsh, C.M. Collins, S.P. Saari, J.E. Zufelt, A.B. Gelvin, and J.W. Hug** (2005c) Energetic residues from live-fire detonations of 120-mm mortar rounds. U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, ERDC/CRREL Technical Report TR-05-15.

## APPENDIX 2-A: MUNITIONS DATA

Table 2-A-1 contains information relevant to the munitions used during the tests covered in this report. Table 2-A-2 contains data on the explosive load of the test components. Propellant charges are given in Table 2-1 (page 2-5). The amount of propellant used per round can and did vary throughout the tests.

<b>Table 2-A-1. Munitions data.</b>					
<b>NSN</b>	<b>DODIC</b>	<b>Nomenclature</b>		<b>Lot No.</b>	<b>Drawn for tests</b>
1310011493185	B643	Cartridge, 60-mm HE, M888, w/fuze, PD, M935		MA00K061001	25
1315005637067	C256	Cartridge, 81-mm HE, M274A3, w/fuze, PD, M576		MA84B153025	40
1315001437048	C226	Cartridge, 81-mm IL, M301A3, w/fuze, time, M84A1		LOW85C108013	61

Notes: Drawn from Fort Richardson Ammo Supply Point 17 Jan 06  
Data from DA Form 5515: Training Ammunition Control Document S/N 1017041

<b>Table 2-A-2. Explosives loads prior to detonation: Impact plume test.</b>					
<b>Munition</b>	<b>DODIC</b>	<b>Energetics quantities (g)</b>			
		<b>RDX</b>	<b>TNT</b>	<b>HMX</b>	<b>Lead azide</b>
Cartridge, 60 mm, M888	B643	215	140	0	0
Fuze, point detonating, M935	N342	15	0	0	0.2

## APPENDIX 2-B: FIRING POINT DATA

Table 2-B-1 contains sampling data, analytical data, and final results for the 60-mm firing point test. The analytical and final results are for NG, the only constituent recovered from the samples.

**Table 2-B-1. 60-mm mortar firing position data.**

Number FRAM-06	Plume	<b>SAMPLING</b>				Decision Unit Descriptor	<b>PROCESSING</b>			<b>FILTRATE ANALYSES</b>		<b>SOOT ANALYSES</b>		<b>RESULTS</b>				
		Area (m <sup>2</sup> )	Field Rep.	# Incrs.	Scoop Area (m <sup>2</sup> )		Filtrate Vol. (mL)	AcN for Filters (mL)	# Filters	SPE Extract (µg/L)	Filtrate Conc. (µg/L)	Mass in Snow (µg)	Filter Extract (µg/L)	Mass on Filter (µg)	Mass in Sample (µg)	Per Unit Area (µg/m <sup>2</sup> )	Total Mass (µg)	
3	FP-LCP	158	1	38	0.0225	0.855	Plume-Surface	2120	1	20	876	8.76	19	412	8.2	27	19	4900
4	FP-LCP	158	2	41	0.0225	0.9225	Plume-Surface	2540	1	20	93	0.93	2.4	270	5.4	8	8.4	1300
5	FP-LCP	158	3	40	0.0225	0.9	Plume-Surface	2500	1	20	121	1.21	3.0	416	8.3	11	13	2000
6	FP-LCP	158	4	77	0.01	0.77	Plume-Surface	2120	1	20	52	0.52	1.1	129	2.6	4	4.8	760
7	FP-LCP	158	1	38	0.01	0.38	Plume-Subsurf	880	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
8	FP-LCP	158	2	41	0.01	0.41	Plume-Subsurf	1030	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
9	FP-LCP	158	3	40	0.01	0.4	Plume-Subsurf	1050	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
10	FP-LCP	168	1	71	0.01	0.71	OTP 0-3 m	2390	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
11	FP-LCP	168	2	73	0.01	0.73	OTP 0-3 m	3010	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
12	FP-LCP	169	3	80	0.01	0.8	OTP 0-3 m	3010	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
13	FP-LCP	220	1	72	0.01	0.72	OTP 3-6 m	2720	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
14	FP-LCP	220	2	69	0.01	0.69	OTP 3-6 m	2760	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
15	FP-LCP	220	3	75	0.01	0.75	OTP 3-6 m	3120	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
16	FP-LCP	77	1	60	0.01	0.6	15-m Transect	1200	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
17	FP-LCP	77	2	60	0.01	0.6	15-m Transect	1220	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
18	FP-LCP	77	3	60	0.01	0.6	15-m Transect	1190	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
19	FP-LCP	100	1	60	0.01	0.6	25-m Transect	1400	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
20	FP-LCP	100	2	60	0.01	0.6	25-m Transect	1240	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
21	FP-LCP	100	3	60	0.01	0.6	25-m Transect	1310	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
22	FP-LCP	70	1	50	0.01	0.5	35-m Transect	1580	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
23	FP-LCP	70	2	50	0.01	0.5	35-m Transect	1420	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
24	FP-LCP	70	3	50	0.01	0.5	35-m Transect	1760	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
25	FP-LCP	100	1	55	0.01	0.55	50-m Transect	1760	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
26	FP-LCP	100	2	50	0.01	0.5	50-m Transect	1660	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—
27	FP-LCP	100	3	50	0.01	0.5	50-m Transect	1680	1	20	-ND-	<0.2	-ND-	-ND-	-ND-	—	—	—

Table 2-B-2 contains sampling data, analytical data, and final results for the 81-mm firing point test. The analytical and final results are for NG, the only constituent recovered from the samples.

**Table 2-B-2. 81-mm mortar firing position data.**

Number FRAM-06	<b>SAMPLING</b>						<b>PROCESSING</b>			<b>FILTRATE ANALYSES</b>			<b>SOOT ANALYSES</b>			
	Plume	Area (m <sup>2</sup> )	Field Rep.	# Incrs.	Scoop Area (m <sup>2</sup> )	Sampled Area (m <sup>2</sup> )	Decision Unit Descriptor	Filtrate Vol. (mL)	AcN for Filters (mL)	SPE Extract (µg/L)	Filtrate Conc. (µg/L)	Mass in Snow (µg)	Filter Extract (µg/L)	Mass on Filter (µg)	Mass in Sample (µg)	
28A*								2390		1,000,000	10,000	23,900				
28B*								2390		1,100,000	11,000	26,290				
28C*								2390		1,000,000	10,000	23,900				
28 (AVE)	FP-UCP	135	1	42	0.0225	0.945	Plume-Surface	2390	1	20	1,033,333	10,333	24,697	19,000,000	380,000	404,697
29	FP-UCP	135	2	42	0.0225	0.945	Plume-Surface	3520	1	20	680,000	6,800	23,936	13,000,000	260,000	283,936
30 AVE	FP-UCP	135	3	44	0.0225	0.99	Plume-Surface	3710	1	20	820,000	8,200	30,422	18,000,000	360,000	390,422
30A*								3710		790,000	7,900	29,309				
30B*								3710		850,000	8,500	31,535				
30C*								3710		820,000	8,200	30,422				
31	FP-UCP	135	1	42	0.01	0.42	Plume-Subsurf	1640	1	20	500,000	5,000	8,200	2,200,000	44,000	52,200
32	FP-UCP	135	2	42	0.01	0.42	Plume-Subsurf	1630	1	20	290,000	2,900	4,727	2,000,000	40,000	44,727
33	FP-UCP	135	3	44	0.01	0.44	Plume-Subsurf	1500	1	20	390,000	3,900	5,850	1,100,000	22,000	27,850
34	FP-UCP	155	1	58	0.01	0.58	OTP 0-3 m	1890	1	20	17,000	170	321	12,000	240	561
35	FP-UCP	155	2	57	0.01	0.57	OTP 0-3 m	2000	1	20	22,000	220	440	16,000	320	760
36	FP-UCP	155	3	64	0.01	0.64	OTP 0-3 m	1890	1	20	24,000	240	454	95,000	1,900	2,354
37	FP-UCP	210	1	51	0.01	0.51	OTP 3-6 m	1880	1	20	4,200	42	79	3,400	68	147
38	FP-UCP	210	2	53	0.01	0.53	OTP 3-6 m	2030	1	20	4,300	43	87	6,100	122	209
39	FP-UCP	210	3	48	0.01	0.48	OTP 3-6 m	1870	1	20	5,100	51	95	6,200	124	219
40	FP-UCP	50	1	60	0.01	0.6	15-m Transect	1400	1	20	4,900	49	69	3,700	74	143
41	FP-UCP	50	2	60	0.01	0.6	15-m Transect	1320	1	20	5,000	50	66	5,800	116	182
42	FP-UCP	50	3	60	0.01	0.6	15-m Transect	1820	2	40	6,900	69	126	3,000	120	246
43	FP-UCP	71	1	60	0.01	0.6	25-m Transect	1140	1	20	4,300	43	49	15,000	300	349
44	FP-UCP	71	2	60	0.01	0.6	25-m Transect	1070	1	20	660	6.6	7.1	540	11	18
45	FP-UCP	71	3	60	0.01	0.6	25-m Transect	1280	1	20	920	9.2	12	610	12	24
46	FP-UCP	84	1	50	0.01	0.5	35-m Transect	2120	1	20	640	6.4	14	950	19	33
47	FP-UCP	84	2	50	0.01	0.5	35-m Transect	2540	4	80	430	4.3	11	160	13	24
48	FP-UCP	84	3	50	0.01	0.5	35-m Transect	2760	1	20	550	5.5	15	910	18	33
49	FP-UCP	61	1	53	0.01	0.53	50-m Transect	2020	1	20	190	1.9	3.8	300	6	10
50	FP-UCP	61	2	51	0.01	0.51	50-m Transect	1970	1	20	280	2.8	5.5	330	6.60	12
51	FP-UCP	61	3	55	0.01	0.55	50-m Transect	2810	1	20	240	2.4	6.7	440	8.80	16

Note: \*A, B, and C are triplicate 500-mL aliquots of the filtrate that were concentrated by solid phase extraction and analyzed for QC purposes.

## **APPENDIX 2-C: BURN POINT DATA**

Table 2-C-1 contains sampling data, analytical data, and final results for the propellant burn point test. The analytical and final results are for NG, the only constituent recovered from the samples.

**Table 2-C-1. Propellant burn point data.**

\*IN 15 M TRANSECT

## APPENDIX 2-D: IMPACT POINT SAMPLE DATA

Table 2-D-1 contains sampling data, analytical data, and final results for the 60-mm HE impact plumes test. The analytical and final results are for RDX, the only constituent recovered from the samples.

**Table 2-D-1. Impact plume data.**

Number FRAM-06	SAMPLING						PROCESSING		FILTRATE ANALYSES			SOOT ANALYSES		RESULTS				
	Plume	Area (m <sup>2</sup> )	Field Rep.	# Incrs.	Scoop Area (m <sup>2</sup> )	Sampled Area (m <sup>2</sup> )	Decision Unit Descriptor	Filtrate Vol. (mL)	AcN for Filters (mL)	SPE Extract (µg/L)	Filtrate Conc. (µg/L)	Mass in Snow (µg)	Filter Extract (µg/L)	Mass on Filter (µg)	Mass on Snow (µg)	Per Unit Area (µg/m <sup>2</sup> )	Total Mass (µg)	
52	1	233	1	83	0.01	0.83	Plume-Surface	1100	1	20	12	0.12	0.14	2.1	0.042	0.18	0.21	50
53	1	233	2	90	0.01	0.90	Plume-Surface	1300	1	20	30	0.30	0.39	1	0.02	0.41	0.45	100
54	1	233	3	100	0.01	1.00	Plume-Surface	1380	1	20	38	0.38	0.53	<1	-ND-	0.53	0.53	120
55	1	200	1	100	0.01	1.00	OTP 0-3 m	970	2	40	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
56	1	200	2	95	0.01	0.95	OTP 0-3 m	900	2	40	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
57	1	200	3	92	0.01	0.92	OTP 0-3 m	980	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
58A	2						-	1960	-	-	7.4	0.074	0.15	-	-	-	-	-
58B	2						-	1960	-	-	7.6	0.076	0.15	-	-	-	-	-
58C	2						-	1960	-	-	6.1	0.061	0.12	-	-	-	-	-
58-AVG	2	200	1	47	0.0225	1.06	Plume-Surface	1960	1	20	7.0	0.070	0.14	5.6	0.11	0.25	0.24	47
59	2	200	2	44	0.0225	0.99	Plume-Surface	1550	1	20	9.3	0.093	0.14	7.8	0.16	0.30	0.30	60
60	2	200	3	48	0.0225	1.08	Plume-Surface	1720	1	20	8.4	0.084	0.14	2.6	0.053	0.20	0.18	36
61	2	200	1	47	0.01	0.47	Plume-Subsurf	1390	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
62	2	200	2	39	0.01	0.39	Plume-Subsurf	1790	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
63	2	200	3	41	0.01	0.41	Plume-Subsurf	1340	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
64	2	286	-	49	0.01	0.49	OTP 0-3 m	740	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
65	3	207	1	100	0.01	1.00	Plume-Surface	1400	1	20	39	0.39	0.54	22	0.44	0.98	0.98	200
66	3	207	2	100	0.01	1.00	Plume-Surface	1320	1	20	38	0.38	0.50	14	0.28	0.78	0.78	160
67	3	207	3	100	0.01	1.00	Plume-Surface	1500	1	40	53	0.53	0.80	7.1	0.28	1.1	1.1	220
68	3	194	-	53	0.01	0.53	OTP 0-3 m	1130	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
69	4	201	1	91	0.01	0.91	Plume-Surface	1460	1	20	10	0.10	0.14	<1	-ND-	0.14	0.16	31
70	4	201	2	94	0.01	0.94	Plume-Surface	1550	1	20	13	0.13	0.21	3.2	0.064	0.27	0.29	58
71	4	201	3	91	0.01	0.91	Plume-Surface	1370	1	20	11	0.11	0.15	1.5	0.03	0.18	0.20	40
72	4	192	-	56	0.01	0.56	OTP 0-3 m	700	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-ND-	-ND-	-
73	5	228	1	99	0.01	0.99	Plume-Surface	1190	1	20	27	0.27	0.32	1.6	0.032	0.35	0.35	81
74	5	228	2	99	0.01	0.99	Plume-Surface	1420	1	20	15	0.15	0.21	1.2	0.024	0.23	0.24	54
75	5	228	3	100	0.01	1.00	Plume-Surface	1250	1	20	15	0.15	0.18	1	0.02	0.20	0.20	46
76	5	194	-	60	0.01	0.60	OTP 0-3 m	1340	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
77	6 & 7	360	1	82	0.01	0.82	Plume-Surface	1110	1	20	14	0.14	0.15	<1	-ND-	0.15	0.19	67
78	6 & 7	360	2	103	0.01	1.03	Plume-Surface	1650	1	20	18	0.18	0.29	<1	-ND-	0.29	0.28	100
79	6 & 7	360	3	112	0.01	1.12	Plume-Surface	1720	1	20	18	0.18	0.31	<1	-ND-	0.31	0.28	100
80	6 & 7	360	4	115	0.01	1.15	Plume-Surface	2900	1	20	11	0.11	0.32	1	0.02	0.34	0.30	110
82	6 & 7	360	6	92	0.01	0.92	Plume-Surface	2400	1	20	12	0.12	0.28	1.4	0.028	0.31	0.33	120
81-AVG	6 & 7	360	5	94	0.01	0.94	Plume-Surface	2140	1	20	14	0.14	0.29	1.9	0.038	0.33	0.35	120
81A							-	2140	-	-	13	0.13	0.28	-	-	-	-	-
81B							-	2140	-	-	13	0.13	0.29	-	-	-	-	-
81C							-	2140	-	-	14	0.14	0.30	-	-	-	-	-
83	6 & 7	238	1	97	0.01	0.97	OTP 0-3 m	1490	2	40	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
84	6 & 7	238	2	67	0.01	0.67	OTP 0-3 m	720	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-
85	6 & 7	238	3	52	0.01	0.52	OTP 0-3 m	570	1	20	-ND-	<0.035	-ND-	-ND-	-ND-	-	-	-

### **3 Sampling of Various Types of Firing Point Areas for Propellant Residues at Several Army Installations**

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#### **Abstract**

Multi-increment soil samples were collected at firing point areas at several different types of army training ranges. These ranges included two antitank rocket ranges, a 155-mm howitzer firing point, areas where 40-mm rifle grenades were fired, an 81-mm mortar firing point, and several small arms firing points. Samples also were collected at an urban demolition range. Depth profile samples were collected at several of these ranges as well. We also placed aluminum-foil-covered pans in front of several areas where 155-mm howitzers, 40-mm grenades, LAW rockets, AT-4 rockets, and small arms were fired, and collected the propellant residues for microscopic analysis.

The most frequently encountered energetic compound in these samples was nitroglycerin (NG). NG was present in surface soils at 40-mm grenade firing points in the low mg/kg range, at antitank firing range firing points at concentrations up to 1000 mg/kg, at or below low mg/kg concentrations at artillery firing points, and at concentrations ranging up to 500 mg/kg at small arms firing points. A few soil samples were analyzed for nitrocellulose and the concentration was generally four to six times that found for NG. Multi-increment samples collected with soil corers with a diameter as small as 2 cm provided reproducible samples from firing point areas. Sample masses as small as 250 g (dry weight basis) were adequate unless the mean concentration was below 1 mg/kg.

#### **Introduction**

Over the past six years, a substantial body of research has been conducted on the deposition of explosives-related energetic residues from the detonation of various military munitions. Much of this work recently has been summarized by Jenkins et al. (2006). Research also has been conducted on the deposition of propellant-related energetic residues at firing points. This work has been supported by the Strategic Environmental Research Program (SERDP) Project ER-

1155, The Canadian Department of National Defence, the U.S. Army Garrison Alaska (USAG-AK), and the Corps of Engineers Distributed Source Program.

The initial studies on propellant deposition were conducted by Jenkins et al. (2001) and Walsh et al. (2004) on deposition of residues from the firing of 105-mm howitzers at Fort Lewis, Washington, and Fort Greely, Alaska. In both cases, residues were found to contain 2,4-DNT, the energetic plasticizer used in some single-base propellants. Subsequent research revealed that these 105-mm residues were deposited as discrete particles that were fibrous in nature (Walsh et al. 2004). The nature of these residues made it difficult to obtain representative soil samples at these firing points by collecting discrete samples using classical grid-node sampling procedures (Walsh et al. 2003). Also, standard sample processing techniques developed for explosives residues at ammunition plants and depots (SW846 Method 8330) were unsuccessful in providing adequately reproducible subsamples for analysis (Walsh et al. 2003).

Studies also were conducted at antitank rocket firing points at Yakima Training Center (YTC), Washington (Pennington et al. 2002); Fort Bliss, Texas (Pennington et al. 2003); Canadian Force Base Gagetown (Thiboutot et al. 2003, 2004); Canadian Force Base Valcartier (Jenkins et al. 2004); and Canadian Force Base Petawawa (Brochu et al. 2006). Nitroglycerin (NG) was present with the highest concentrations at locations behind the firing line due to the back blast of these shoulder-fired rockets.

Less research has been conducted on propellant residues from 155-mm artillery and mortars. Initial sampling conducted at 155-mm firing points at YTC indicated that concentrations of propellant-related residues were below analytical detection limits (Pennington et al. 2002). Similar results were obtained in studies conducted by the U.S. Army Environmental Center at Fort Bliss (USACHPPM 2004) and at Fort Polk, Louisiana (USACHPPM in press). A subsequent study conducted by M.R. Walsh et al. (2005) on a snow-covered range at Donnelly Training Center showed that 2,4-DNT was deposited from single-base (green bag) propellant, but that concentrations were much lower than from 105-mm howitzers.

To our knowledge, only a recent publication addresses propellant residues at small arms ranges (Brochu et al. 2006). This report provides some initial results for several small arms ranges at Canadian Force Base Petawawa. At both pistol and rifle ranges, 2,4-DNT was found in surface soils with a maximum concentration of 9.6 mg/kg and 2.3 mg/kg, respectively. Surprisingly, NG was not detected at these ranges for samples collected in 2004, although it was detected in subsequent sampling at these ranges (Brochu, personal communication).

## Objectives

The overall objective of this research effort is to develop a better understanding of propellant deposition at Army training ranges during firing practice with a number of different munition systems, including 40-mm rifle grenades, 81-mm mortars, 66-mm M-72 LAW rockets, AT-4 rockets, 155-mm howitzers, and small arms (50-caliber machine gun, 5.62-mm rifle, 9-mm pistol, and 7.62-mm rifle). To accomplish a portion of this task, multi-increment soil samples were collected in areas where training with specific weapons had been conducted. When possible, soil profile samples also were collected to try to understand the downward mobility of the various propellant chemicals. Attempts also were made on several ranges to capture residues during firing activities for microscopic analysis.

Specific objectives were to determine the mass of sample and the number of increments per sample required to provide adequately representative samples to characterize the mean concentration within exposure units at various types of firing point areas. To investigate these questions, multi-increment samples with different numbers of increments were collected within given exposure areas at antitank rocket firing points using corers with different diameters.

## Methods

### *Soil Sample Collection at Yakima Training Center*

This portion of the study was conducted from 19 to 23 May 2006 at Yakima Training Center (YTC), Washington. Soil samples were collected at firing point areas at ranges 7, 8, 15, 26, and the MPRC (Multi-Purpose Range Complex). Because troop training took precedence over this research effort, the areas sampled and the time for sampling at each area were based on availability. In some cases, we collected samples just after troop training was completed. In other cases, we sampled ranges not scheduled for use on that day. Specific information for each sampling effort is described below. The corers used for sample collection in this study (Fig. 3-1) were designed and built at CRREL (Walsh 2004).

### **Range 26: Area used for 40-mm rifle grenade practice**

We collected samples at range 26 on 19 May 2006 as a squad of Special Forces soldiers trained with 40-mm rifle grenades (Fig. 3-2). The first sampling area was in front of a firing position where 250 rounds of 40-mm grenades were fired (200 blue-capped practice rounds and 50 gold-capped high-explosive- [HE] filled rounds). The firing line was immediately adjacent to the fence used to

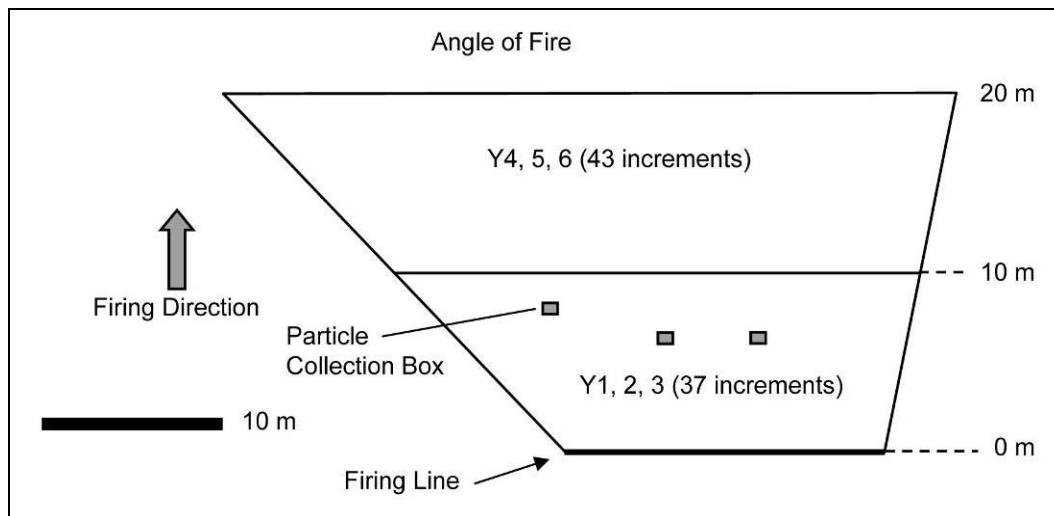
isolate the central impact area at YTC. The area immediately in front of the firing activity was divided into two zones, 0 to 10 m and 10 to 20 m downrange from the firing activity. In this case, the area selected for sampling was based on the direction of fire that the troops used for selected targets downrange.



**Figure 3-1. Coring tool designed at CRREL for multi-increment sample collection.**



**Figure 3-2. Special Forces training at range 26 with 40-mm rifle grenades.**



**Figure 3-3. Sampling layout at range 26, Yakima Training Center, Washington. 40-mm grenades (200 practice, 50 filled with M203 HE) were fired at this location. Samples were collected with the 3-cm coring tool.**

Triplicate multi-increment samples were collected using a systematic-random design (Fig. 3-3) in each of these two sampling areas (samples Y1, Y2, and Y3 in the 0- to 10-m zone and samples Y4, Y5, and Y6 in the 10- to 20-m zone). The number of increments in each sample varied from 37 for samples Y1, Y2, and Y3 to 43 for samples Y4, Y5, and Y6. These samples were collected using a 3-cm-diameter corer from a depth of 0 to 2.5 cm below surface.

In addition to the soil samples, we attempted to collect propellant residues for microscopic analysis by placing three cardboard boxes at distances ranging from 6.8 to 7.8 m downrange. These boxes were in place during the firing of the 50 rounds of HE-filled 40-mm grenades. After the firing, the contents of the boxes were emptied into a plastic bag, although no particles were visually observed.

The second area sampled at range 26 was quite a distance farther away from the central impact area than the initial area sampled, where there was no visual indication that the area had been used for previous firing activities. Here, the Special Forces fired 160 rounds of 40-mm white star cluster flares. Because the flares were fired in a much more vertical orientation than the 40-mm practice and HE-filled grenades, only one 10-m × 10-m area was flagged and sampled (Fig. 3-4). In this area, triplicate 30-increment samples (samples Y7, Y8, and Y9) were collected with the 3-cm corer from 0 to 2.5 cm in depth.



Figure 3-4. Special Forces training with 40-mm white star cluster flares.

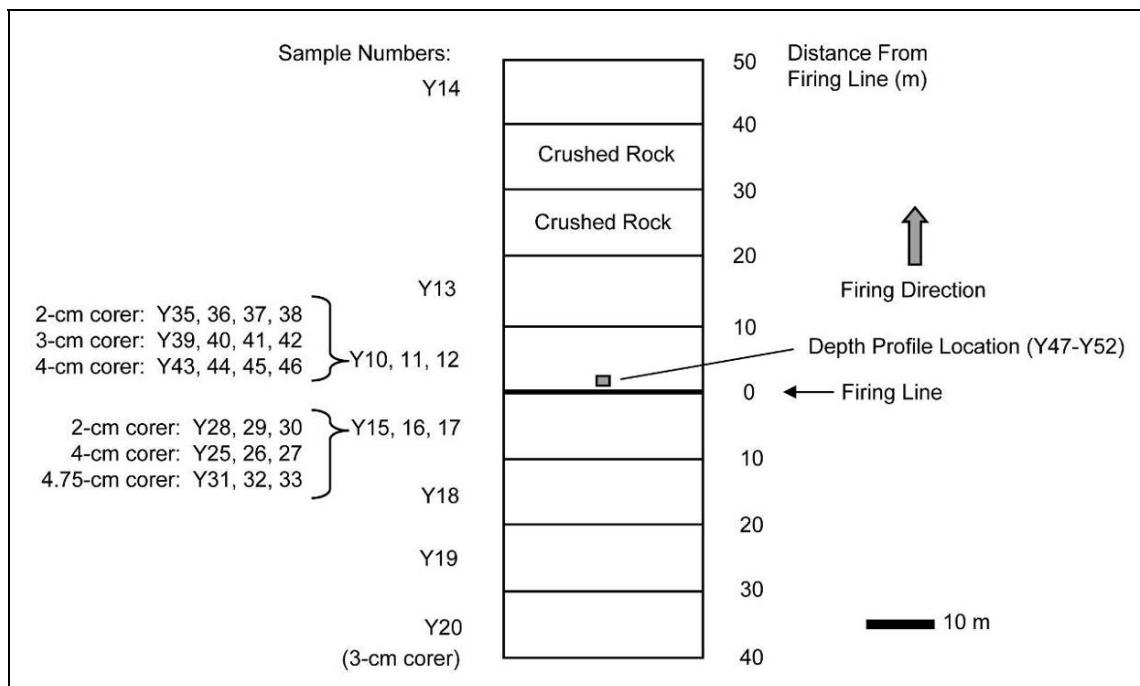


Figure 3-5. YTC range 8 used for practice with 40-mm grenades.

#### Range 8: Range used for practice with 40-mm grenades

A 30-m section of the firing line was selected that encompassed several foxholes and other areas where firing activities were conducted (Fig. 3-5). Sampling areas were located using measuring tapes to a distance of 50 m between the firing line and the target and 40 m behind the firing line (Fig. 3-6).

Samples were collected in 10-m-deep zones along this 30-m line from 0 to 10 m, 10 to 20 m, and 40 to 50 m in front of the firing line (samples Y10 to Y14) and from 0 to 10 m, 10 to 20 m, 20 to 30 m, and 30 to 40 m behind the firing line (samples Y15 to Y20) on 19 and 20 May 2006. Samples were not collected in zones from 30 to 40 m and 40 to 50 m in front of the firing line because this area was covered with crushed rock. Samples were not collected beyond 40 m behind the firing line because the range was bounded by a fence beyond this distance, with a road located behind the fence.



**Figure 3-6. Sampling layout at range 8, YTC. This range was used for practice with 40-mm grenades and LAW rockets. Samples were collected using coring tools with 2-, 3-, 4-, and 4.75-cm diameters from the surface to 2.5-cm depth. All samples comprised 50 increments.**

Within each of these zones, 50-increment samples were collected using a 3-cm-diameter corer from the 0- to 2.5-cm depth. Triplicate samples were collected in the 0- to 10-m zones in front of and behind the firing lines and single samples were collected in the other zones.

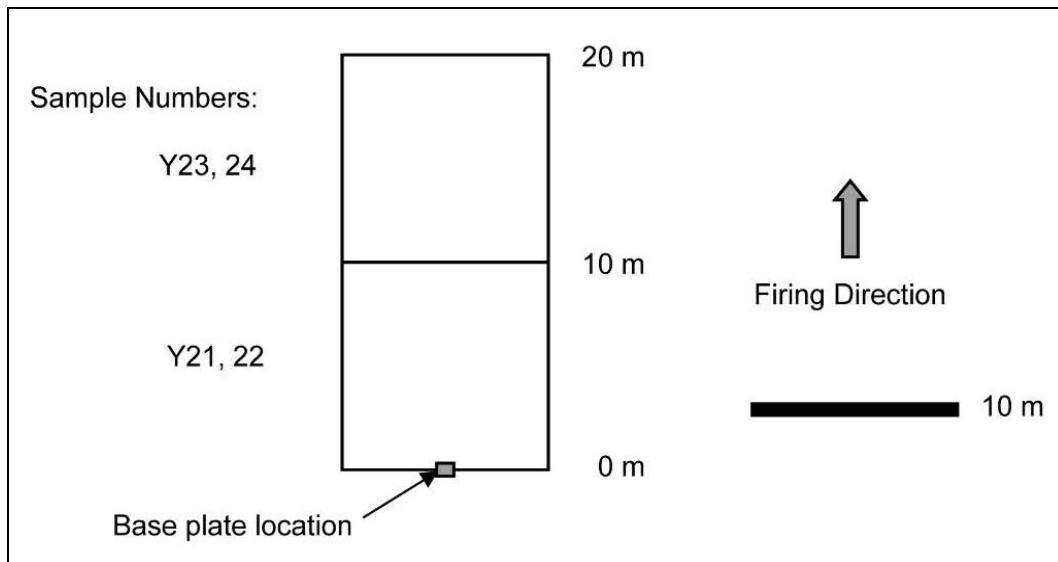
Within the 0- to 10-m zone behind the firing line, additional sets of triplicate samples were collected. These samples were also 50-increment samples collected within the 0- to 2.5-cm depth, but were collected with several corers having diameters of 2 cm (samples Y28–Y30), 4 cm (samples Y25–Y27), and 4.75 cm

(samples Y31–Y33). An additional 50-increment subsurface sample (sample 34) also was collected within this zone from 2.5 to 5 cm in depth using the 4.75-cm corer below surface sample Y31.

Similarly, on the afternoon of 21 May 2006, an additional set of samples was collected within the 0- to 10-m zone in front of the firing line at range 8. Quadruplicate 50-increment samples were collected with three different diameter corers (2-, 3-, and 4-cm diameters) from the 0- to 2.5-cm depth (samples Y35 to Y46). Depth profile samples also were collected within this zone with depths ranging from 0 to 28 cm (samples Y47 to Y52).

#### MPRC: Mortar firing position

On the morning of 20 May 2006, we were shown an area where 81-mm mortar firing had taken place overnight. The indentation in the soil where the base plate had been positioned was located and the direction of firing identified. Two sampling grids were marked using measuring tapes in an area 0 to 10 m and 10 to 20 m from the firing position and 5 m to either side of the base plate indentation (Fig. 3-7). In each of these grids duplicate 40-increment samples were collected from the 0- to 2.5-cm depth using the 3-cm-diameter corer (samples Y21 to Y24).



**Figure 3-7. Sampling layout at an 81-mm mortar firing location, MPRC, YTC. Samples (each with 40 increments) were collected the morning after a night-time firing exercise with the 3-cm-diameter corer from the surface to 2.5-cm depth.**

**Range 7: Range used for practice with 40-mm grenades and HE-filled LAW and AT-4 rockets**

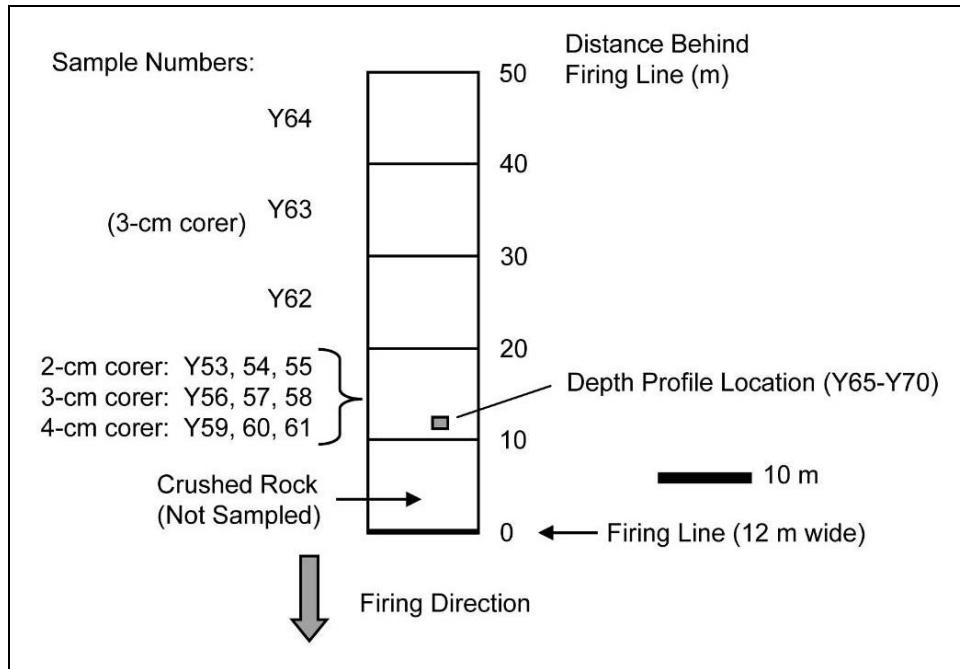
On 22 May, we accompanied a squad of soldiers training with HE-filled 66-mm M-72 LAW and AT-4 rockets. Prior to the firing of seven LAW rockets, the troops identified a 12-m firing line from which they would fire along the fence line separating the firing position from the impact area. We deployed a set of seven plastic disposable painting trays lined with aluminum foil from about 15 to 30 m behind the firing line in an attempt to capture propellant residues for microscopic analysis. After the firing was completed, we recovered these trays, carefully folded the aluminum foil to retain whatever residue was present, and relined the trays with fresh aluminum foil. The trays were redeployed prior to the firing of a single AT-4 rocket, after which the trays again were recovered and the aluminum foil folded to retain any residue that had been deposited.

After firing was complete, the area behind the 12-m-long firing line was divided into several sampling grids at the following distances: 10–20 m, 20–30 m, 30–40 m, and 40–50 m. The zone from 0 to 10 m was a gravel road and was not sampled. Within each of these 12-m × 10-m zones (Fig. 3-8), 45-increment samples were collected from 0- to 2.5-cm depth using a 3-cm-diameter corer (samples Y56–Y58 and Y62–Y64). Within the 10- to 20-m zone, triplicate samples were collected and within the remaining zones a single sample was collected. We collected two additional sets of 45-increment triplicate samples within the 10- to 20-m grid. The first set was collected using the 2-cm-diameter corer (samples Y53–Y55) from the 0- to 2.5-cm depth and the second set was collected using the 4-cm-diameter corer (samples Y59–Y61) from the same depth. A set of six depth profile samples also was collected from the surface to 30 cm at a position 12 m behind the firing line (samples Y65 to Y70). These samples were collected by digging a trench with a folding shovel and sampling the undisturbed sidewall using a stainless steel scoop.

**Range 15: Small arms firing area**

Range 15 is used to train troops mounted in various types of vehicles. The units engage a simulated enemy and various small arms are fired at a variety of targets. Several specific areas where these firing activities take place were identified and multi-increment samples were collected using the 3-cm-diameter corer from a depth of 0 to 2.5 cm.

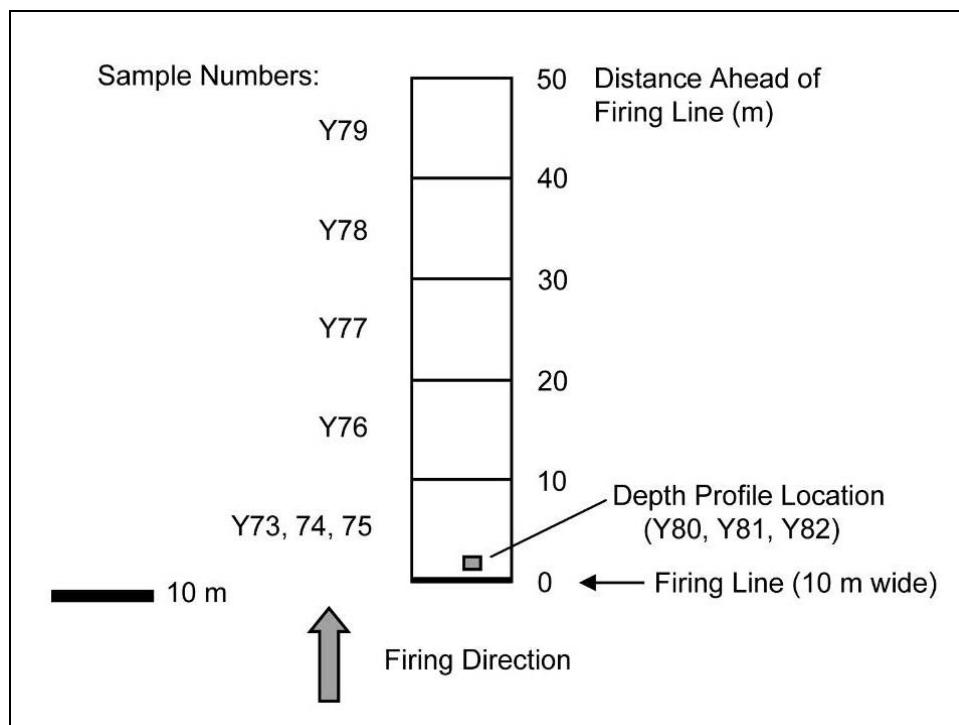
The first engagement area was along a 10-m strip located 5 to 8 m from the road. Firing activity is commonly conducted in this area (sample Y71). The second area was located because several hundred empty shells were found along the road in an area not normally used for firing. A 40-increment sample was collected 3 to 5 m from the road in the direction of fire (sample Y72).



**Figure 3-8. Sampling layout at range 7, YTC.** This range was used for practice with 66-mm M-72 LAW and AT-4 rockets. Samples were collected using the 3-cm-diameter corer from all four decision units between 10 and 50 m behind the firing point (comprising 45 increments of soil from 0- to 2.5-cm depth). Within the zone between 10- and 20-m distance, additional triplicate samples were collected with 2- and 4-cm-diameter coring tools.

The third area sampled was a site where troops entering range 15 conduct their initial firing from a gravel pad. At this location, the firing area is a fixed position about 10 m wide; sampling zones of the following distances from the pad oriented downrange were flagged using measuring tapes: 0–10 m, 10–20 m, 20–30 m, 30–40 m, and 40–50 m (Fig. 3-9). A set of 36-increment samples was collected within these zones; triplicate samples within the 0- to 10-m zone and single samples within the other zones (samples Y73 to Y79).

At 2 m in front of the firing line, a set of three depth profile samples was collected. The ground was very hard in this area. A hole was dug with a folding shovel and samples were collected from the sidewall using a stainless steel scoop. Samples were collected from 9 to 14 cm (sample Y80), 5 to 9 cm (sample Y81), and from 0 to 5 cm (sample Y82).



**Figure 3-9. Sampling layout at YTC small arms range 15. Location is in an area where initial firing tests are conducted upon entering the range. Samples (each with 36 increments) were collected with the 3-cm-diameter corer from the surface to 2.5-cm depth.**

#### Range 4: Small arms firing area

At range 4, dismounted small arms firing is conducted. Here, a 36-increment sample (sample Y83) was collected along a 10-m portion of the firing line in an area located 0 to 10 m ahead of the firing line. The 3-cm-diameter corer was used and increments were collected from the 0- to 2.5-cm depth.

#### *Sample Collection at Fort Lewis (FL), Washington*

This study was conducted from 20 to 22 June 2006 at Fort Lewis, Washington. Soil samples were collected at firing point areas at ranges 59, 62, 93, 93Z, and Firing Point 3409. Again, troop training took precedence over this research effort; areas sampled and the time available at each range were based on availability. In some cases, we collected samples just after troop training was completed. In other cases, we sampled ranges not scheduled for use on that day. Specific information for each sampling effort is described below.



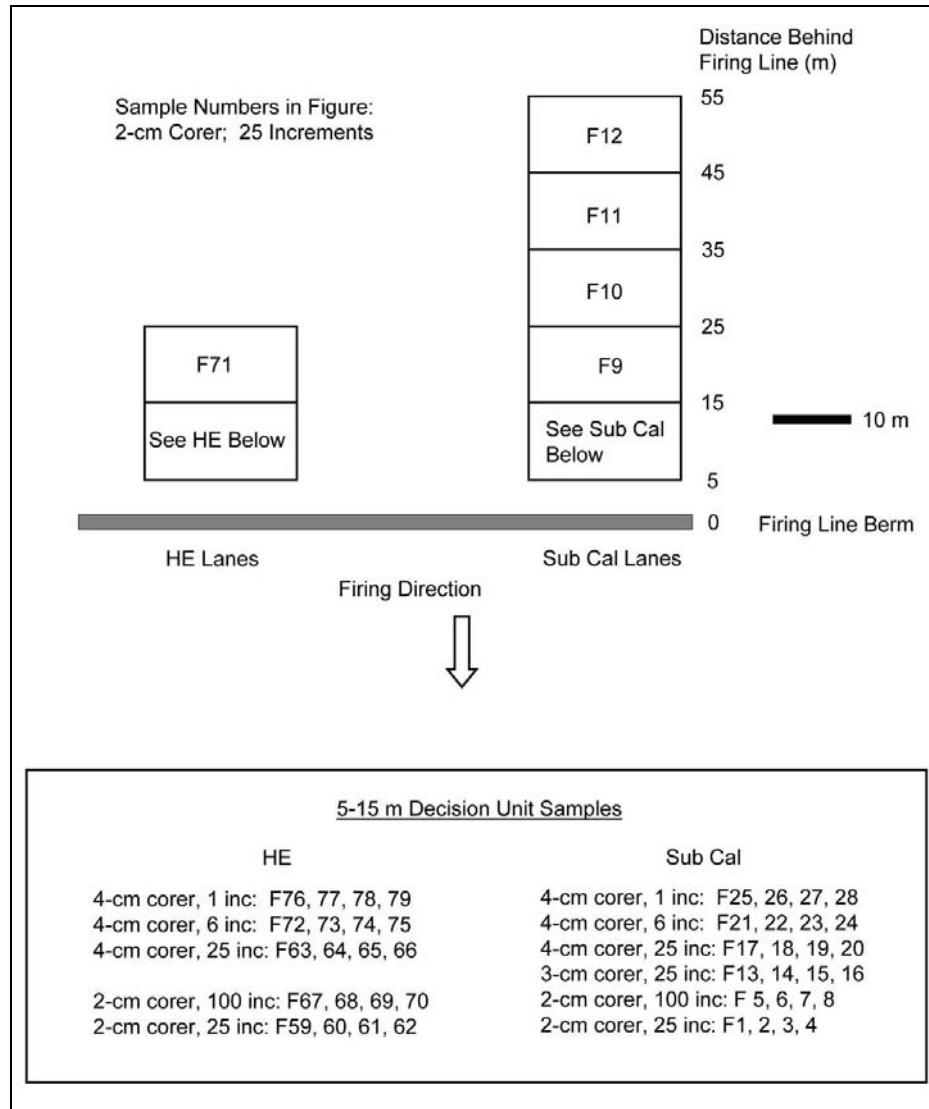
**Figure 3-10. Fort Lewis range 59 used for training with LAW and AT-4 rockets. View is from the sub-cal section of the berm of the flat area behind the firing line where samples were collected.**

#### **Range 59: LAW and AT-4 rocket range**

We sampled two firing point areas at range 59; both areas were relatively flat grassy areas (Fig. 3-10). The first was the area used for firing training rockets (sub-cal) that did not contain high explosive (HE) and the second was the live-fire area. The sub-cal area was sampled on 20 June and the specific area sampled was 5 to 55 m behind the firing line. The area behind the firing line was chosen for sampling because the major propellant residue deposition is found in this area for shoulder-fired rockets, including the 66-mm M72 Light Anti-armor Weapon (LAW) and the 84-mm AT-4 (Jenkins et al. 2005).

The firing line was located on a berm that was a few meters higher than the area behind the firing line. Soil samples were collected in 20-m-wide areas that were 5–15 m, 15–25 m, 25–35 m, 35 to 45 m, and 45–55 m behind the firing line. The area from 0 to 5 m was not sampled because it was on a steep slope off the berm. Within the 5- to 15-m area, a series of soil samples was collected, all from the 0- to 2.5-cm depth (Fig. 3-11). All were multi-increment samples collected using a systematic-random sampling strategy because of the known difficulty in collecting representative samples using discrete samples (Jenkins et al. 2006). Quadruplicate samples with variations in the following parameters were collected: number of increments (1, 6, 25, 100); core diameter (2, 3, 4 cm);

and positioning (systematic-random collection path, diagonal central line running from the near left corner to the far right corner, and at the grid midpoint) (Table 3-1). The grid midpoint samples were intended to approximate a contiguous sample and were collected by removing six 4-cm-diameter cores from adjacent locations (Fig. 3-12).



**Figure 3-11. Sampling layout at range 59, Fort Lewis, Washington.** This range was used for practice with AT-4 rockets. Decision units were 20 m wide and 10 m long starting at 5 m from the firing line. Quadruplicate samples were collected using the 2-, 3-, and 4-cm-diameter corer as shown in the sample number listings.

**Table 3-1. Sampling strategy utilized at Fort Lewis LAW and AT-4 rocket training range 59 in the decision unit 5–15 m from the firing point.**

Core diameter (cm)	Increments	Pattern	Sample numbers	
			Sub-cal	HE
2	25	systematic-random	F1, 2, 3, 4	F59, 60, 61, 62
2	100	systematic-random	F5, 6, 7, 8	F67, 68, 69, 70
3	25	systematic-random	F13, 14, 15, 16	—
4	25	systematic-random	F17, 18, 19, 20	F63, 64, 65, 66
4	6	diagonal line <sup>1</sup>	F21, 22, 23, 24	F72, 73, 74, 75
4	1	central position <sup>2</sup>	F25, 26, 27, 28	F76, 77, 78, 79

<sup>1</sup> Six increments collected along a diagonal line from the near left corner to the far right corner.  
<sup>2</sup> Collected with a grouping of six contiguous cores in the center of the decision unit.

A single 25-increment sample was collected in the remaining grids in this sub-cal area using a systematic-random pattern and the 2-cm-diameter corer from 15 to 25 m (sample L9), 25 to 35 m (sample L10), 35 to 45 m (sample L11), and 45 to 55-m (sample L12).

The second area sampled at this range was behind the firing area used when live HE-containing AT-4 rockets were fired; this location was about 30 m away from the sub-cal area (Fig. 3-11). Samples were also collected from the 0- to 2.5-cm depth. At this location samples were collected only in the area from 5 to 15 m and 15 to 25 m behind the firing line. A similar series of samples was collected as described for the 5- to 15-m area behind the sub-cal area, but no samples were collected with the 3-cm-diameter corer (see Figure 3-11).

Quadruplicate samples were collected in this area using the systematic-random design using the following strategies: 25-increment samples using the 2-cm-diameter corer (samples L59 to 62), 25-increment samples using the 4-cm-diameter corer (samples L63 to 66), 100-increment samples using the 2-cm-diameter corer (samples L67 to 70), 6-increment samples using the 4-cm-diameter corer (samples L72 to 75) that were collected along a diagonal line from the left front to the right back of the grid, and 1-increment samples collected at the midpoint of the grid using six 4-cm-diameter cores from adjacent areas (to approximate a contiguous sample) (samples L76 to 79). Sample L71 was collected in the area from 15 to 25 m behind the firing line using the 2-cm corer (25 increments).



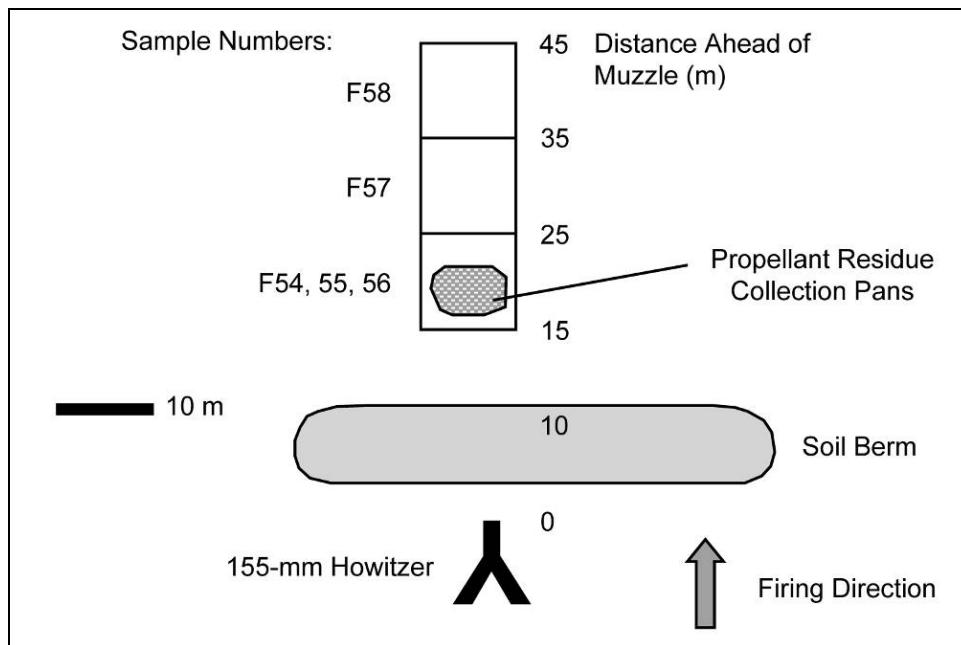
**Figure 3-12.** Layout of contiguous sampling at range 59, Fort Lewis, Washington, for simulating a single discrete sample with six 4-cm-diameter cores. Quadruplicate samples were collected from the center of the 20-m × 10-m decision unit positioned 5–15 m behind the firing line.

#### Firing point 3409

Firing point 3409 was an area where the ROTC had been training over the summer months. In this area, four 155-mm howitzers were deployed and fired in a fixed position for several weeks prior to our sampling (Fig. 3-13). M1 propellant, composed of 85% nitrocellulose (NC) and 10% nitroglycerin (NG), was being used (green bag M3A1).



**Figure 3-13.** Fort Lewis firing point 3409, at location of 155-mm howitzer, in front of which live-fire residues and soil samples were collected. Arrow marks sampled area beyond the gravel berm.



**Figure 3-14. Sampling layout at Fort Lewis firing point FP 3406.** The 155-mm howitzer at this site was used throughout the summer for ROTC practice. Three 10-m × 10-m decision units were established starting 15 m from the muzzle along the line of fire, beyond a soil berm. Soil samples with 30 increments were collected with a 2-cm-diameter corer penetrating to 2.5-cm depth. Samples of propellant residue also were collected in 13 aluminum-foil-covered pans within the closest decision unit.

During the afternoon of 20 June we deployed 13 aluminum-foil-covered pans in front of a single 155-mm howitzer at distances ranging from 16 to 23 m in front of the muzzle (Fig. 3-14). ROTC troops fired the howitzer throughout the day of 21 June; we recovered the pans on the morning of 22 June. The aluminum foil was folded to contain any residue that was present and the samples were shipped back to the laboratory.

Surface soil samples also were collected on 22 June in the area in front of the howitzer where the pans had been deployed (Fig. 3-14). The area was on the far side of a large soil berm positioned about 7 m from the muzzle (Fig. 3-13). A 10-m-wide zone, centered on the muzzle and perpendicular to the line of fire, was flagged starting about 15 m from the muzzle. The area was divided into three grids from 15 to 25 m, 25 to 35 m, and 35 to 45 m along the line of fire. These grids were heavily vegetated with a variety of shrubs and grasses. Within the 15- to 25-m area, triplicate 30-increment systematic-random samples were collected from the 0- to 2.5-cm depth using a 2-cm-diameter corer (samples L54 to L56).

Single samples using the same strategy were collected in the 25- to 35-m zone (sample L57) and the 35- to 45-m zone (sample L58).

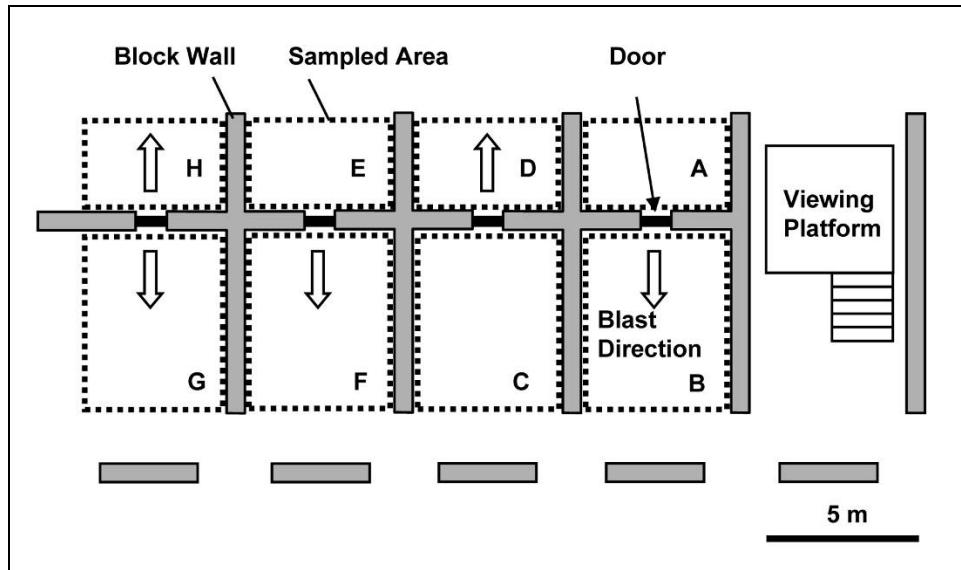
#### **Range 62: Urban breaching range**

On 21 June we were allowed to sample range 62, an urban breaching range (Fig. 3-15). A troop unit had finished training at the range just prior to our sampling. The unit's training exercise involved setting up small detonations to destroy doors using detonation (det) cord to enable entry into locked rooms. To the knowledge of the troops taking part, only detonation cord is used at this range because they thought that C4 would destroy the training facility's walls.



**Figure 3-15. Fort Lewis range 62 used for urban breaching training.**

Range 62 is divided into a series of rooms with connecting doorways, as shown in Fig. 3-16. We collected surface soil samples in each room using stainless steel scoops from the 0- to 2.5-cm depth. In all cases 25-increment samples were collected using the systematic-random sampling design (samples L29 to L38). The surface material in these rooms appeared to be gravel fill and was totally unvegetated. Triplicate samples were collected within room G; single samples were collected in the other seven rooms.



**Figure 3-16. Sampling layout at Fort Lewis urban breaching range 62.** Soil samples at this site comprise 25 increments collected with stainless steel scoops to a 2.5-cm depth. Single samples were obtained in each room, except room G, where triplicate samples were collected.

#### Range 93Z: Machine gun range

Machine gun range 93Z was sampled on 21 June (Fig. 3-17). The firing line at this range is about 25 m wide. Grids were flagged at distances from 0 to 5 m, 5 to 10 m, and 10 to 15 m across the entire 25-m width (Fig. 3-18). Within the 0- to 5-m grid, triplicate 35-increment samples were collected from the 0- to 2.5-cm depth using a 2-cm-diameter corer using the systematic-random sampling design (samples L39 to L41). A single sample was collected using the same strategy in the 5- to 10-m and the 10- to 15-m grids (samples L42 and L43, respectively).

#### Range 93: Small arms range

Range 93 is another small arms range where training is conducted by firing various types of small arms at pop-up targets from foxholes along individual lanes (Fig. 3-19). We selected three lanes in the center of the range for sampling and flagged a 5-m-wide area at distances of 0 to 5 m and 5 to 10 m downrange of each of the foxholes (Fig. 3-20). All samples consisted of 25 increments, collected using the 2-cm-diameter corer from the 0- to 2.5-cm depth using the systematic-random design. For the firing position on the left (lane 2), a single sample was collected in the 0- to 5-m (sample L44) and 5- to 10-m (sample L45) grids. For the two grids in the center position (lane 3), triplicate samples were collected from the 0- to 5-m grid (samples L46 to L48) and from the 5- to 10-m grid (samples L49 to L53). A single sample was collected from the 0- to 5-m grid (sample L52) and 5- to 10-m grid (sample L53) from the firing position on the right (lane 4).



Figure 3-17. Fort Lewis range 93Z used for machine gun training.

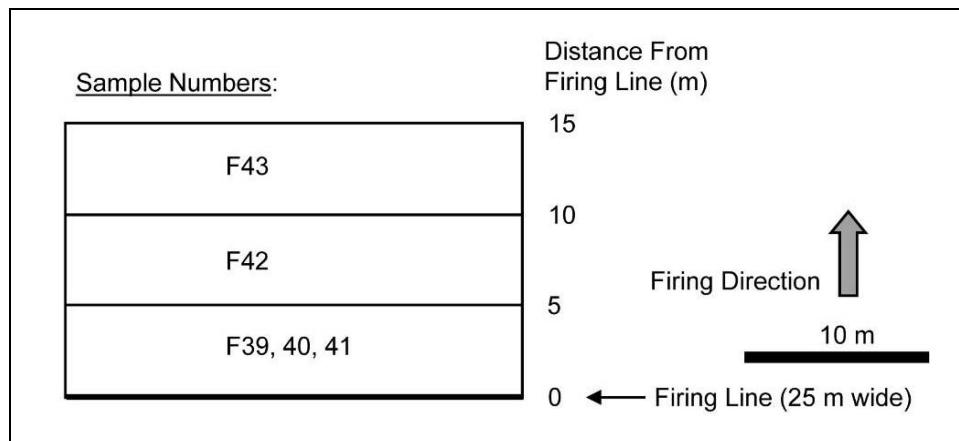
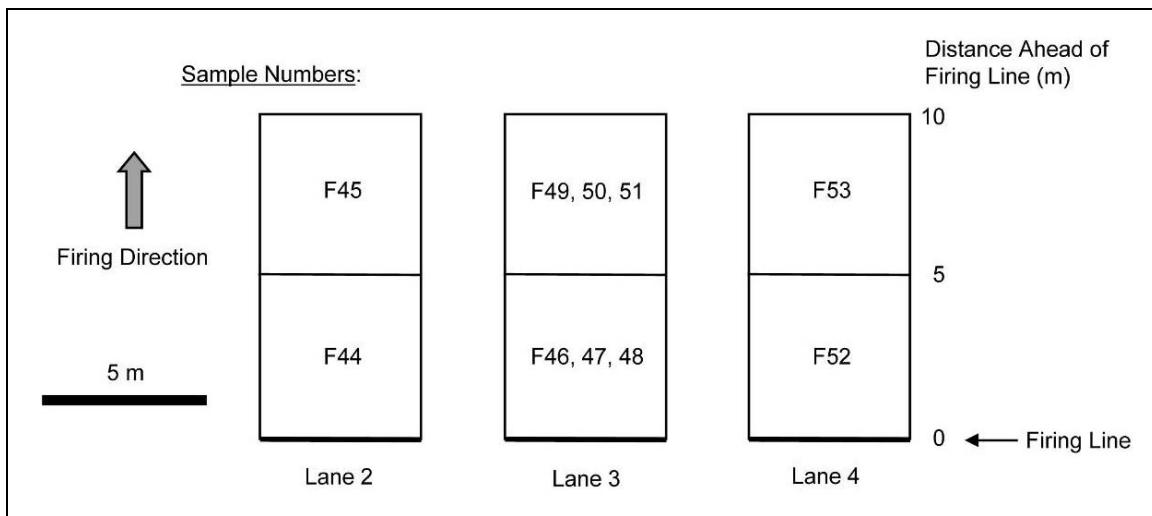


Figure 3-18. Sampling layout at machine gun range 93Z, Fort Lewis. Samples were collected using the 2-cm-diameter corer with 35 increments of soil from 0- to 2.5-cm depth. Triplicate samples were obtained in the 0- to 5-m decision unit and single samples were obtained in the other two decision units.



**Figure 3-19. Sampling layout at Fort Lewis small arms range 93. Samples (each with 25 increments) were collected with the 2-cm-diameter corer from the surface to 2.5-cm depth.**



**Figure 3-20. Foxholes at Fort Lewis range 93 used for small arms training.**

### *Sample Collection at Fort Benning (FB), Georgia*

Samples were collected at Fort Benning, Georgia (FB) at artillery firing point 4 on Cactus Road on 21 June 06 (Fig. 3-21). Three 100-increment surface soil samples (0 to 5 cm) were collected from a 100-m × 100-m grid where the artillery is positioned and fired (samples B1 to B3).



**Figure 3-21. Artillery firing point 4 on Cactus Road at Fort Benning, Georgia.**

### *Soil Sample Processing*

All soil samples from YTC, FL, and FB were returned to CRREL by overnight carrier. Samples were air-dried in the laboratory and passed through a 10-mesh (2-mm) sieve to remove oversized material. For the multi-increment samples, the <2-mm fraction was ground on a Lab TechEssa LM2 (LabTech Essa Pty. Ltd., Bassendean, WA, Australia) puck-mill grinder for 60 seconds five times with a 60-second cooling period between grinds. Grinding reduced the particle size of the material to a flour (<70 µm). After grinding, samples were mixed thoroughly and spread to form a 1-cm-thick layer; subsamples were obtained by collecting 30 increments randomly through the entire thickness of the layer of ground material to obtain a subsample mass of about 10 g. Triplicate

laboratory subsamples were obtained from the ground soil samples from one out of every five samples processed.

The entire <2-mm fraction of the soil profile samples was extracted with acetonitrile using a ratio of solvent (mL) to soil (g) of about 2 to 1.

#### **Soil sample extraction and analysis for propellants and explosives**

The 10-g portions of soil for the multi-increment samples and the soil samples from the profile samples were extracted on a shaker table for 18 hours using 20 mL of acetonitrile. The extracts were filtered by passing each through a Millex-FH PTFE 0.45 syringe filter (Millipore Corp.). For reverse-phase high-performance liquid chromatography (HPLC) analysis, this extract was diluted 1 to 3 with deionized water to match the solvent strength of the HPLC eluent.

HPLC analysis was conducted on a modular RP-HPLC system from Thermo Finnigan composed of a SpectraSYSTEM Model P1000 isocratic pump, a SpectraSYSTEM UV2000 dual wavelength UV/VIS absorbance detector set at 210 and 254 nm (cell path 1 cm), and a SpectraSYSTEM AS300 auto sampler. Samples were introduced by over-filling a 100- $\mu$ L sampling loop. Separations were made on a 15-cm  $\times$  3.9-mm (4- $\mu$ m) NovaPak C-8 column (Waters Chromatography Division, Milford, Massachusetts) maintained at 28°C and eluted with 15:85 isopropanol/water (v/v) at 1.4-mL/min. Concentrations were estimated from peak heights compared to commercial multi-analyte standards (Restek). Detection limits for RP-HPLC analyses were 0.02 mg/kg except for NG, which had a detection limit of 0.05 mg/kg. The target analytes for RP-HPLC analysis were the 14 energetic compounds of SW846 Method 8330 (USEPA 1994) with the addition of nitroglycerin and PETN. Analyte identities were confirmed for selected samples using a 15-cm  $\times$  3.9-mm (4- $\mu$ m) NovaPak LC-CN RP-HPLC column (Waters Chromatography Division, Milford, Massachusetts) eluted with 65% water, 25% methanol, and 10% acetonitrile (Jenkins and Golden 1993).

#### **Soil sample extraction and analysis for nitrocellulose**

Selected soil samples were shipped to ERDC-EL in Omaha, Nebraska, for determination of NC.

##### *Determination of Nitrocellulose at ERDC-EL (Omaha laboratory)*

All chemicals, reagents, and solvents were obtained from Fisher Scientific (Pittsburgh, Pennsylvania) unless otherwise noted. Standard solutions were prepared from NC (12% nitrogen) (Aldrich, St. Louis, Missouri) that was dried to constant weight in a vacuum desiccator in the dark. Dried NC (4.166 g) was dissolved in acetone (Burdick and Jackson, Muskegon, Michigan) to give a final

concentration of 4.17 g/L NC. Nitrocellulose control samples were prepared by spiking 10 g Ottawa sand with 1.0 mL NC standard solution for a final NC concentration of 417 mg/kg (nitrogen equivalent concentration for NC with 12% nitrogen content is 50 mg/kg) or nitrogen as nitrate/nitrite concentration of 20 mg/L in the hydrolysate. The sand was rinsed with acetone and allowed to dry prior to addition of the standard solution. The spiking solvent was also allowed to evaporate from the control samples prior to proceeding. The soils were dried, sieved, and ground as described above.

For control and soil samples, 10 g sand or soil was stirred at 30 rpm on a rotary stirrer with 10 mL ultra pure water for 10 min. For field samples expected to have high concentrations of NC present, 0.5- to 2.0-g samples were used to minimize dilution of the final extract. The stirred samples were centrifuged by using a swinging bucket rotor at moderate speed for 10 min or until the supernatants were clear, after which the supernatants were decanted and discarded. The water rinse step was repeated once. A 10-mL aliquot of ethanol (VWR International, West Chester, Pennsylvania) was added to each sample after the water rinses. Samples were stirred for 10 min on a rotary stirrer at 30 rpm and centrifuged at moderate speed for another 10 min or until the supernatants were clear. The ethanol layer was decanted and discarded. Acetone (15 mL) was then added to each sample, and the samples were again stirred and centrifuged as described previously for the water and ethanol washes. Once the supernatant was clear, it was decanted and reserved in a clean 50-mL polypropylene centrifuge tube. The acetone extraction was repeated and the extracts combined. The extract was evaporated to dryness under a gentle stream of forced air. The dried extracts were combined with 5 mL 5N sodium hydroxide, and the vials were placed in a boiling water bath for 10 min. After cooling, the hydrolyzed samples were diluted with 20 mL ultra pure water and adjusted to below pH 8 by bubbling a flow (approximately 2 L/min) of industrial grade (98.5%) compressed carbon dioxide (Linweld, Lincoln, Nebraska), after which the sample was diluted to a final volume of 25 mL with ultra-pure water.

The hydrolysates were analyzed for nitrate and nitrite according to Method 300.1 (U.S. EPA 1999) by using a Dionex (Sunnyvale, California) DX-120 ion chromatograph equipped with a Dionex AS14 Ionpak column and a conductivity detector. The mobile phase was 0.5M carbonate:0.5M bicarbonate and the flow rate was 1.8 mL/min. Injection volume was 50  $\mu$ L. Potassium nitrate and sodium nitrite were used as standards and were obtained from Mallinckrodt Laboratory Chemicals (Phillipsburg, New Jersey). The nitrocellulose concentration was calculated from the sum of the concentrations of nitrate and nitrite and the percentage of NC nitrogen content. For quality control samples, the percent

nitrogen provided by the vendor was used for the calculation. For field samples, a nitrogen percentage of 14% was used.

#### **Microscopic analysis of propellant residues**

Propellant residues collected from pans positioned in front of and behind firing activities at YTC and FL were examined at CRREL. Using a Wild 2 stereomicroscope, we sorted through the residue collected for each type of round and separated out likely propellant residues from any soil present. Candidate particles were photographed and then a representative particle was placed in a 20-mL scintillation vial with 1.0 mL of acetonitrile and allowed to stand overnight. The following day, an aliquot of the acetonitrile was added to a known quantity of water and the solution analyzed by RP-HPLC using an LC-8 column and the separation described previously (15% isopropanol, 85% water).

## **RESULTS AND DISCUSSION**

### **QA/QC**

A variety of quality assurance measures was taken to ensure that the quality of data obtained in this study was adequate to draw conclusions from these samples. This included collection and analysis of replicate field samples to assess whether the samples collected in the field were representative of the areas sampled, and collection and analysis of replicate subsamples from laboratory-processed samples to ensure that subsamples taken for extraction were representative of the sample. Blank samples also were processed to ensure that any target analytes detected in field samples were not due to laboratory contamination. Laboratory control samples (LCS) were prepared and analyzed by adding known amounts of target analytes to blank samples and carrying these LCS samples through the entire analytical process to ensure that target analytes were not lost due to sample processing.

Overall, nitroglycerin (NG) was the target analyte detected in most of the samples from these firing point areas. 2,4-DNT was detected in several ranges as well. Thus, the discussion of results from QC samples will center on NG and 2,4-DNT concentrations.

### **Blank soils and laboratory control samples**

Results from the analysis of blank and LCS samples are presented in Table 3-2. Four blank samples were mechanically ground, subsampled, extracted with acetonitrile, and analyzed by RP-HPLC-UV along with the field samples from Yakima Training Center (YTC). Three blank samples were processed and

analyzed in an identical manner along with the field samples from Fort Lewis (FL) and Fort Benning (FTB). The nitroglycerin (NG) and 2,4-DNT concentrations found for six of these seven blank samples were below detection limits of 0.05 and 0.02 mg/kg, respectively. The NG concentration for the seventh sample was 0.08 mg/kg. The extract for this sample was analyzed just after sample number 83 from YTC that had by far the highest NG concentration of any sample from that installation (85 mg/kg); thus, the small but measurable concentration for this blank sample was probably due to a small amount of carryover from the previous sample. The concentration for this blank was only one one-thousandth of that for sample 83; however, the next highest sample concentration for YTC was only 8.6 mg/kg. A similar percent carryover from that sample would result in a concentration that would be less than the detection limit of 0.05 mg/kg.

The percent recovery estimates for NG in the four LCS samples were 101, 101, 94.2, and 88.4% (Table 3-2), indicating that the recovery of NG taken through the analytical process was excellent. Similarly, the recovery for 2,4-DNT was 97.8, 96.0, 94.4, and 92.8% in the four LCS samples. Recovery of the other Method 8330 target analytes ranged from 78.6 to 103%, except for tetryl, where recoveries ranged from 70.4 to 121% (Table 3-2). These results indicate that if other target analytes had been present above analytical detection limits in these samples , they would have been detected.

### **Subsampling variability**

Triplicate subsamples were analyzed for about 20% of the soil samples collected at YTC and FL (Table 3-3). Measured mean NG concentrations in these samples varied from 0.06 mg/kg to 1400 mg/kg (four samples had concentrations less than the detection limit of 0.05 mg/kg for all three replicates), and the RSD for the triplicates ranged from 0.51% to 25.0%. The overall mean relative standard deviation for NG in the 23 sets of triplicates where concentrations were above the detection limit was 7.70%, even though the mean concentrations for two of these samples were less than a factor of two higher than the detection limit. These results are excellent and indicate the sample processing and subsampling method adequately represented the field samples.

2,4-DNT was detected in only two of the 29 sets of laboratory triplicates. In one case the mean concentration was 0.07 mg/kg and yet the % RSD was only 4.4%. In the other sample, the mean concentration was 3.00 mg/kg, and the RSD was 2.00%. In the other 27 sets, the 2,4-DNT concentration was less than a detection limit of 0.02 mg/kg in all three replicate subsamples of each. These results are consistent with results reported by Walsh et al. (in press), who developed this processing and subsampling approach.

**Table 3-2. Results from analysis of laboratory control samples and blanks for nitroglycerin, 2,4-DNT, and other energetic target analytes.**

Sample	Type	Concentration (mg/kg)											
		HMX	RDX	TNB	DNB	TNT	Tetryl	NG	2ADNT	4ADNT	2,4-DNT	2,6-DNT	PETN
<b>A. QA Samples processed with field samples from Yakima Training Center</b>													
LCS-1	<b>Spiked conc.</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	<b>Determined conc.</b>	0.986	0.918	1.01	0.960	1.02	1.21	1.01	1.03	0.988	0.978	0.904	
	<b>% Recovery</b>	98.6	91.8	101	96	102	121	101	103	98.8	97.8	90.4	
LCS-2	<b>Spiked conc.</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	<b>Determined conc.</b>	0.972	0.902	0.972	0.942	0.978	1.02	1.01	0.992	0.966	0.960	0.908	
	<b>% Recovery</b>	97.2	90.2	97.2	94.2	97.8	102	101	99.2	96.6	96.0	90.8	
Blank 1								<0.05			<0.02		
Blank 2								<0.05			<0.02		
Blank 3								<0.05			<0.02		
Blank 4								0.08*			<0.02		
<b>B. QA Samples processed with field samples from Fort Lewis and Fort Benning</b>													
Blank 5								<0.05			<0.02		
Blank 6		0.042	0.05		0.022			<0.05			<0.02		
Blank 7								<0.05			<0.02		
LCS-3	<b>Spiked conc.</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	<b>Determined conc.</b>	0.936	0.876	0.944	0.938	0.812	0.732	0.942	0.946	0.946	0.944	0.920	0.966
	<b>% Recovery</b>	93.6	87.6	94.4	93.8	81.2	73.2	94.2	94.6	94.6	94.4	92.0	96.6
LCS-4	<b>Spiked conc.</b>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
	<b>Determined conc.</b>	0.960	0.890	0.974	0.924	0.926	0.912	0.884	0.946	0.912	0.928	0.852	0.974
	<b>% Recovery</b>	96.0	89.0	97.4	92.4	92.6	91.2	88.4	94.6	91.2	92.8	85.2	97.4

\* This sample was analyzed following the highest concentration sample (85 mg/kg) in this study from YTC.

**Table 3-3. Concentrations of nitroglycerin and 2,4-DNT in laboratory replicate subsamples.**

Site	Sample	Rep	NG			2,4-DNT		
			Concentration (mg/kg)	Mean (mg/kg)	% RSD	Concentration (mg/kg)	Mean (mg/kg)	% RSD
YTC	5	1	1.87	1.79	5.14	<0.01		
		2	1.82			<0.01		
		3	1.69			<0.01		
	10	1	1.06	1.05	5.63	<0.01		
		2	1.10			<0.01		
		3	0.98			<0.01		
	15	1	0.31	0.33	5.16	<0.01		
		2	0.34			<0.01		
		3	0.34			<0.01		
	20	1	<0.05			<0.01		
		2	<0.05			<0.01		
		3	<0.05			<0.01		
	25	1	0.21	0.24	16.6	<0.01		
		2	0.22			<0.01		
		3	0.28			<0.01		
	30	1	0.31	0.35	16.7	<0.01		
		2	0.32			<0.01		
		3	0.41			<0.01		
	35	1	1.33	1.32	5.91	<0.01		
		2	1.39			<0.01		
		3	1.23			<0.01		
	40	1	1.08	1.28	19.4	<0.01		
		2	1.20			<0.01		
		3	1.56			<0.01		
	45	1	1.13	1.42	25.0	<0.01		
		2	1.32			<0.01		
		3	1.82			<0.01		
	55	1	5.18	5.16	3.31	<0.01		
		2	4.98			<0.01		
		3	5.32			<0.01		
	60	1	7.94	8.20	4.29	<0.01		
		2	8.06			<0.01		
		3	8.60			<0.01		
	64	1	0.08	0.09	9.87	<0.01		
		2	0.09			<0.01		
		3	0.10			<0.01		
	71	1	<0.05			<0.01		
		2	<0.05			<0.01		
		3	<0.05			<0.01		
	75	1	1.65	1.62	10.8	<0.01		
		2	1.78			<0.01		
		3	1.44			<0.01		
	79	1	0.07	0.06	23.6	<0.01		
		2	0.08			<0.01		
		3	0.05			<0.01		

**Table 3-3 (cont'd). Concentrations of nitroglycerin and 2,4-DNT in laboratory replicate subsamples.**

Site	Sample	Rep	NG			2,4-DNT		
			Concentration (mg/kg)	Mean (mg/kg)	% RSD	Concentration (mg/kg)	Mean (mg/kg)	% RSD
FL	5	1	598	581	2.76	<0.01		
		2	566			<0.01		
		3	580			<0.01		
	10	1	80.4	82.4	2.86	<0.01		
		2	81.8			<0.01		
		3	85.0			<0.01		
	15	1	600	575	11.4	<0.01		
		2	624			<0.01		
		3	500			<0.01		
	20	1	588	587	0.71	<0.01		
		2	590			<0.01		
		3	582			<0.01		
	25	1	197	208	4.75	<0.01		
		2	216			<0.01		
		3	212			<0.01		
	30	1	<0.05			<0.01		
		2	<0.05			<0.01		
		3	<0.05			<0.01		
	35	1	<0.05			<0.01		
		2	<0.05			<0.01		
		3	<0.05			<0.01		
	40	1	7.42	7.29	3.17	0.072		
		2	7.02			0.066		
		3	7.42			0.070	0.07	4.41
	45	1	276	275	0.84	2.94		
		2	272			3.06		
		3	276			3.00	3.00	2.00
	50	1	240	229	4.03	<0.01		
		2	224			<0.01		
		3	224			<0.01		
	60	1	812	846	3.58	<0.01		
		2	856			<0.01		
		3	870			<0.01		
	65	1	1130	1130	0.51	<0.01		
		2	1120			<0.01		
		3	1130			<0.01		
	70	1	868	859	4.07	<0.01		
		2	820			<0.01		
		3	888			<0.01		
	75	1	1360	1400	2.51	<0.01		
		2	1400			<0.01		
		3	1430			<0.01		
			Max RSD	25.0		Max RSD	4.41	
			Min RSD	0.51		Min RSD	2.00	
			Mean RSD	7.70		Mean RSD	3.20	
			n	23		n	2	

### **Field sampling variability**

Field sample replicates were collected in 17 areas at YTC, 15 areas at FL, and one area at FB (Table 3-4). Some of these replicates were triplicates and some were quadruplicates. Four corer diameters were used for these replicates at YTC: 2 cm, 3 cm, 4 cm, and 4.75 cm. NG was the only target analyte detected in these samples. The relative standard deviation for NG in these sets of replicates varied from 3.94% to 41.7% with a mean value of 16.9%. In only two of the 33 areas sampled was the RSD in excess of 30%. In both of these cases, the mean concentration was less than 0.3 mg/kg. Thus the ability to replicate samples from these firing point areas at all three installations was excellent. Because results indicate that NG concentrations in soil samples collected from these areas were adequately reproducible, we conclude that they were also adequately representative of the mean NG concentration in these sampling areas.

### **Sample mass requirements**

Sampling error is the inability to collect truly representative samples from the areas of concern. This error results from two types of heterogeneity, compositional heterogeneity and distributional heterogeneity, both of which exist at different scales (Pitard 2000). Compositional heterogeneity is due to the fact that not all of the particles that make up the population of particles within the decision unit have the same concentration of target analytes. Thus, a truly representative sample must include all particle sizes in the same proportion as that present within the zone of interest. This heterogeneity is at a maximum when a portion of the target analytes is present as discrete particles, which is often the case for energetic compounds present at firing points on training ranges (Taylor et al. 2004, Jenkins et al. 2005). Error due to compositional heterogeneity is called the fundamental error and is inversely related to the sample mass. Distributional heterogeneity is due to the fact that contaminant particles are scattered across the decision unit unevenly, sometimes with a systematic component as well as a short-range random component. For multi-increment samples, the error associated with distributional heterogeneity is inversely related to the number of individual increments used to build the sample.

As a part of this study, experiments were conducted to determine the sample mass required to overcome compositional heterogeneity and provide reproducible samples at antitank rocket range firing points. In four 10-m × 20-m locations (two at YTC and two at FL), replicate multi-increment samples were collected using soil corers of differing diameters. Thus these corers collected a different mass of soil for each increment collected, and, for equal numbers of increments, provided different sample masses. The corers had diameters of 2 cm, 3 cm, 4 cm, and 4.75 cm. An analysis of the reproducibility as a function of corer diameter

was conducted for field replicates at YTC and FL (Table 3-5). In the first area sampled (area A), 50 increments were collected for each size corer and the grand mean NG concentration for the area was 0.24 mg/kg. The RSD for samples collected with the 2-cm, 3-cm, 4-cm, and 4.75-cm corers were 41.7, 37.9, 25.8, and 25.8%, respectively. For area B, 50 increments also were collected for the 2-cm, 3-cm, and 4-cm corers, and the mean concentration of NG was 1.20 mg/kg. The RSD for the samples collected with the 2-cm, 3-cm, and 4-cm corers was 12.8, 21.6, and 17.0%, respectively (Table 3-5). At area C, 25-increment samples were collected; the mean concentration of NG was 641 mg/kg and the RSD for samples collected with the 2-cm, 3-cm, and 4-cm corers were 9.85, 12.9, and 9.75%. At area D (25 increments), the mean NG concentration was 986 mg/kg; the RSD for the samples collected with the 2-cm corer was 9.5% and the RSD for the samples collected with the 4-cm corer was 13.9%. Thus, only when the concentration of NG was very low (less than 1 mg/kg) was there an apparent improvement in RSD with increasing corer (and mass) size. The mass of soil collected (on a dry weight basis) with the 2-cm corer for the four areas ranged from about 235 to 520 g. This mass appears to be adequate to provide an acceptable level of reproducibility (RSD <30%) for these firing point areas unless the mean concentration is below 1 mg/kg.

#### **Effect of varying numbers of increments**

The contribution of spatial heterogeneity to the total sampling uncertainty can be minimized by increasing the number of increments in each multi-increment sample. To investigate this effect on replicate sample reproducibility, experiments were conducted in two locations at FL antitank rocket range 59. These studies were conducted in a 10-m × 20-m area, 5 to 15 m behind the firing line at the sub-cal firing area (area C) and the high explosives (HE) firing area (area D). As usual, multi-increment samples were collected using a systematic-random design.

Four different strategies were compared. The first was collection of 100-increment samples using the 2-cm-diameter corer. The second was collection of 25-increment samples using the 4-cm-diameter corer. The third was collection of 6-increment samples using the 4-cm-diameter corer with increments collected on a diagonal from one corner of the sampling area to the opposite far corner. The fourth strategy was collection of a 1-increment sample where the single increment was collected in the center of the 10-m × 20-m sampling area. This single increment was made up of six adjoining 4-cm-diameter cores and therefore had a sample mass equivalent to that from the 6-increment samples collected with the 4-cm-diameter corer. There were four replicates for each collection strategy. Different masses of soil were collected for the various strategies. However, as

shown in the previous section for these two sampling areas, the lowest mass collected should be adequate to overcome any contribution from compositional heterogeneity.

For both areas C and D, the % RSD was inversely related to the number of increments in each sample (Table 3-6). For example, in area C the % RSDs for 100-, 25-, 6-, and 1-increment samples were 5.72, 9.75, 18.3, and 31.0%, respectively. The results for area D were quite similar. The RSD for 100-, 25-, 6-, and 1-increment samples at area D were 8.6, 13.8, 21.3, and 23.3%, respectively (Table 3-6). Mean concentrations for the 1-increment samples were also much lower than for the 100-, 25-, and 6-increment samples. The 1-increment samples were collected in the center of each area and clearly this single increment was not adequate to provide a representative sample for the entire area, even though it was a large sample of 350 plus grams. Thus the systematic component of the spatial heterogeneity was not adequately represented using a 1-increment sample from the center of the grid, even when the mass of the single increment was fairly large. When the concentration of the propellant residue was fairly high and all rounds were fired from the same firing position, the 6-increment sample provided an adequate sample (RSD <30%), but increasing the number of increments further substantially reduced the error due to spatial heterogeneity.

It must be acknowledged, though, that compositional and distributional heterogeneity interact so greatly that is difficult, if not impossible, to completely isolate one variable from the other. For propellant residues at this firing area, the distributional portion dominates if the mass collected was adequate. From past research, this spatial component is largely due to the gradient in concentration relative to the distance from the firing point.

### *Antitank Rocket Ranges*

The most common munitions fired at antitank rocket ranges are 66-mm M72 LAW rockets and 84-mm AT-4 rockets. The double-base M7 propellant for the LAW rocket contains 55% nitrocellulose (NC), 35% nitroglycerin (NG), 8% potassium perchlorate, 0.8% ethyl centralite, and 1.2% carbon black (DAC Propellant Identification Guide 2006). The propellant for the AT-4 is also double base (NC/NG), but the exact formulation is proprietary. Two antitank rocket ranges were investigated in this study: range 7 at YTC and range 59 at FL. From research at other antitank rocket ranges we know that the majority of residues at firing points are deposited behind the firing line (Jenkins et al. 2004, 2006). For this reason, and because we were not allowed to sample downrange of the firing line at either range due to safety concerns, all samples at both ranges were collected behind the firing line.

**Table 3-4. Concentrations of nitroglycerin for field replicate samples.**

Sample number	Area sampled	Corer	Increments	NG concentration (mg/kg)	Mean (mg/kg)	% RSD
YTC-1		3-cm	37	3.16	2.81	13.6
YTC-2				2.86		
YTC-3				2.40		
YTC-4		3-cm	43	1.41	1.72	16.2
YTC-5				1.79		
YTC-6				1.95		
YTC-7		3-cm	30	0.28	0.24	28.9
YTC-8				0.28		
YTC-9				0.16		
YTC-10		3-cm	50	1.05	0.91	13.7
YTC-11				0.81		
YTC-12				0.87		
YTC-15	A	3-cm	50	0.33	0.27	37.9
YTC-16				0.15		
YTC-17				0.32		
YTC-25		4-cm	50	0.24	0.21	25.8
YTC-26				0.15		
YTC-27				0.25		
YTC-28		2-cm	50	0.30	0.26	41.7
YTC-29				0.14		
YTC-30				0.35		
YTC-31		4.75-cm	50	0.25	0.21	25.8
YTC-32				0.24		
YTC-33				0.15		
YTC-35	B	2-cm	50	1.32	1.31	12.8
YTC-36				1.48		
YTC-37				1.35		
YTC-38				1.08		
YTC-39		3-cm	50	1.34	1.15	21.6
YTC-40				1.28		
YTC-41				1.18		
YTC-42				0.79		
YTC-43		4-cm	50	1.05	1.13	17.0
YTC-44				1.01		
YTC-45				1.42		
YTC-46				1.05		
YTC-53		2-cm	45	7.00	5.97	15.7
YTC-54				5.76		
YTC-55				5.16		
YTC-56		3-cm	45	5.60	6.16	21.6
YTC-57				5.20		
YTC-58				7.68		
YTC-59		4-cm	45	6.94	7.11	14.2
YTC-60				8.20		
YTC-61				6.20		

**Table 3-4 (cont'd).**

<b>Sample number</b>	<b>Area sampled</b>	<b>Corer</b>	<b>Increments</b>	<b>NG concentration (mg/kg)</b>	<b>Mean (mg/kg)</b>	<b>% RSD</b>			
YTC-62		3-cm	47	0.14	0.10				
YTC-63			48	0.07					
YTC-64			44	0.09		37.7			
YTC-73		3-cm	36	1.98	1.68				
YTC-74				1.45					
YTC-75				1.62		16.1			
<b>Statistics - YTC data</b>				Mean RSD (all data)		22.5			
				Mean RSD (3-cm corer)		23.9			
				Mean RSD (2-cm corer)		23.4			
				Mean RSD (4-cm corer)		19.0			
				RSD (4.75 corer)		25.8			
FL-1	C	2-cm	25	710	623	9.85			
FL-2				612					
FL-3				604					
FL-4				566					
FL-5		2-cm	100	581	591	5.72			
FL-6				558					
FL-7				586					
FL-8				638					
FL-13		3-cm	25	680	660	12.9			
FL-14				616					
FL-15				575					
FL-16				770					
FL-17		4-cm	25	728	641	9.75			
FL-18				606					
FL-19				642					
FL-20				587					
FL-21		4-cm	6	356	486	18.3			
FL-22				556					
FL-23				506					
FL-24				524					
FL-25		4-cm	1	208	189	31.0			
FL-26				250					
FL-27				190					
FL-28				110					
FL-39		2-cm	35	10.7	8.60	21.7			
FL-40				7.29					
FL-41				7.78					
FL-46		2-cm	25	522	504	7.24			
FL-47				528					
FL-48				462					
FL-49		2-cm	25	322	276	16.9			
FL-50				229					
FL-51				276					

**Table 3-4 (cont'd). Concentrations of nitroglycerin for field replicate samples.**

Sample number	Area sampled	Corer	Increments	NG concentration (mg/kg)	Mean (mg/kg)	% RSD		
FL-54		2-cm	30	<0.05				
FL-55				<0.05				
FL-56				<0.05				
FL-59	d	2-cm	25	1020	981	9.5		
FL-60	d			846				
FL-61	d			996				
FL-62	d			1060				
FL-63	d	4-cm	25	1070	1010	13.9		
FL-64	d			808				
FL-65	d			1130				
FL-66	d			1020				
FL-67	d	2-cm	100	760	818	8.6		
FL-68	d			758				
FL-69	d			896				
FL-70	d			859				
FL-72	d	4-cm	6	1200	1120	21.3		
FL-73	d			1030				
FL-74	d			840				
FL-75	d			1400				
FL-76	d	4-cm	1	167	223	23.3		
FL-77	d			232				
FL-78	d			290				
FL-79	d			204				
<b>Statistics - FL Data</b>				Mean RSD (all data)		15.0		
				Mean RSD (3-cm corer)		12.9		
				Mean RSD (2-cm corer)		9.93		
				Mean RSD (4-cm corer)		16.8		
				Mean RSD (25 increments)		10.0		
				Mean RSD (100 increments)		4.76		
				Mean RSD (6 increments)		19.8		
				Mean RSD (1 increment)		27.1		
				MAX		41.7		
				Min		5.72		
<b>Fort Benning</b>								
FB-1		Scoop		2.22	2.39	10.5		
FB-2		Scoop		2.28				
FB-3		Scoop		2.68				
<b>All data</b>		<b>Mean RSD (all data with over 25 increments)</b>				<b>18.0</b>		

**Table 3-5. Concentrations of NG for multi-increment samples collected with various diameter corers.**

Sample number	Area sampled	Sample mass (g)	Corer	Increments	NG		
					Concentration (mg/kg)	Mean (mg/kg)	% RSD
YTC-15	A	1157	3-cm	50	0.33	0.27	37.9
YTC-16		1115			0.15		
YTC-17		1111			0.32		
YTC-25		1838	4-cm	50	0.24	0.21	25.8
YTC-26		1870			0.15		
YTC-27		1804			0.25		
YTC-28		463	2-cm	50	0.30	0.26	41.7
YTC-29		469			0.14		
YTC-5		458			0.35		
YTC-31		2581	4.75-cm	50	0.25	0.21	25.8
YTC-32		2552			0.24		
YTC-33		2659			0.15		
YTC-35	B	525	2-cm	50	1.32	1.31	12.8
YTC-36		534			1.48		
YTC-37		528			1.35		
YTC-38		503	3-cm	50	1.08	1.15	21.6
YTC-39		1250			1.34		
YTC-40		1207			1.28		
YTC-41		1213			1.18		
YTC-42		1236			0.79		
YTC-43		2157	4-cm	50	1.05	1.13	17.0
YTC-44		2184			1.01		
YTC-45		2446			1.42		
YTC-46		2541			1.05		
FL-1	C	220	2-cm	25	710	623	9.85
FL-2		247			612		
FL-3		235			604		
FL-4		240			566		
FL-13		520	3-cm	25	680	660	12.9
FL-14		541			616		
FL-15		525			575		
FL-16		528			770		
FL-17		1128	4-cm	25	728	641	9.75
FL-18		1066			606		
FL-19		1076			642		
FL-20		1159			587		
FL-59	D	317	2-cm	25	1020	981	9.5
FL-60		303			846		
FL-61		287			996		
FL-62		286			1060		
FL-63		1235	4-cm	25	1070	1010	13.9
FL-64		1217			808		
FL-65		1164			1130		
FL-66		1226			1020		

**Table 3-6. Concentrations of NG for multi-increment samples collected with varying numbers of increments at Fort Lewis antitank rocket range 59.**

Sample number	Area sampled	Sample mass (<2 mm, dry wt, g)	Corer	Increments	NG		
					Concentration (mg/kg)	Mean	% RSD
5	C	640	2-cm	100	581	591	5.72
6		637			558		
7		637			586		
8		638			638		
17		1128	4-cm	25	728	641	9.75
18		1066			606		
19		1076			642		
20		1159			587		
21		326	4-cm	6	356	486	18.3
22		316			556		
23		322			506		
24		323			524		
25	D	366	4-cm	1	208	189	31.0
26		356			250		
27		352			190		
28		367			110		
67		1137	2-cm	100	760	818	8.6
68		1167			758		
69		1142			896		
70		1104			859		
63		1235	4-cm	25	1070	1007	13.9
64		1217			808		
65		1164			1130		
66		1226			1020		
72		357	4-cm	6	1200	1120	21.3
73		357			1030		
74		366			840		
75		320			1400		
76		387	4-cm	1	167	223	23.3
77		416			232		
78		328			290		
79		407			204		

At YTC range 7, the area sampled was where an 84-mm AT-4 rocket was fired just prior to our soil sampling. The firing position and the area from 0 to 10 m behind the firing location were gravel and were not sampled. Table 3-7 presents NG results for multi-increment soil samples collected behind the firing line. In the 10- to 20-m zone, triplicate samples were collected using the 2-cm, 3-cm, and 4-cm corers at the depth increment from 0 to 2.5 cm. The mean NG concentration for the nine replicates in the 10- to 20-m zone was 6.42 mg/kg with a relative standard deviation of 17.1%. The NG concentrations in single samples from the 20- to 30-m, 30- to 40-m, and 40- to 50-m zones were 0.14, 0.07, and 0.09 mg/kg, respectively (Fig. 3-22). No other target analytes were reproducibly detected in these samples, although we did detect several non-target analytes in the RP-HPLC-UV chromatograms, subsequently identified as NG breakdown products: 1,2-dinitroglycerin, 1,3-dinitroglycerin, and 1-nitroglycerin. The relatively low concentrations of NG at range 7 were similar to those found in an earlier study at YTC (Pennington et al. 2002), but quite different from those found at most other ranges (see below). The breakdown products have also been identified in unfired propellant. Whether the concentrations found were due to presence in the unfired propellant or due to hydrolysis of NG in soil is under investigation. It should be emphasized that there were no specific firing areas identifiable at range 7. Firing occurs along a fence line that separates the firing area from the impact area. The firing line is at least 50 m in length.

At FL, we sampled two antitank rocket firing point areas at range 59. The first was behind the firing point for the sub-cal (or training rockets) and the second was behind the firing area where the HE-filled rockets were fired. These firing areas are well marked and have a width of about 20 m. NG concentrations found at FL were several orders of magnitude higher than at YTC (Table 3-7). The mean concentration for the samples collected in the area from 5 to 15 m behind the sub-cal area was 632 mg/kg (omitting samples containing only 1 or 6 increments). Concentrations in samples 15–25 m, 25–35 m, 35–45 m, and 45–55 m behind the firing line were 175, 82.4, 13.0, and 3.36 mg/kg, respectively (Fig. 3-23). For the HE firing area, the mean concentration in the area 5 to 15 m behind the firing line was 936 mg/kg and the concentration for the 15- to 25-m area was 206 mg/kg.

These FL results are quite similar to the concentrations found at antitank rocket ranges at three Canadian installations. At Canadian Force Base (CFB)-Valcartier, the mean concentration in the 5- to 15-m area behind the firing line was 788 mg/kg and the mean concentration for the area from 15 to 25 m was 339 mg/kg (Jenkins et al. 2004). At CFB-Petawawa, concentrations were obtained at two distances behind the firing line (Brochu et al. 2006). The mean concentration from 0 to 10 m behind the firing line was 2400 mg/kg and from 10 to 20 m

behind the firing line it was 380 mg/kg. A second antitank rocket range at CFB-Petawawa was also sampled. Researchers were told that this range had been closed for 30 years and yet the mean NG concentration in surface soil was still 250 mg/kg. At CFB-Gagetown, NG concentrations were as high as 6560 mg/kg at a distance of 2 m behind the firing line (Thiboutot et al. 2004). The NG concentrations in surface soils at an antitank range at Schofield Barracks, Hawaii, also were high—1400 mg/kg in the 0- to 10-m area behind the firing line and 14 mg/kg in the 10- to 20-m area (Hewitt et al. 2004).

The two-order-of-magnitude difference in NG concentrations between surface soils at YTC and FL was surprising. FL receives much more rainfall, yet has a much higher NG concentration, which indicates that the difference cannot be due to dissolution and leaching of NG from the propellant residues at YTC. The results from Petawawa indicate that, once deposited, NG is quite persistent in surface soils. We believe that the large difference in NG concentrations at the YTC and FL antitank ranges is due either to a large difference in the number of rockets fired at these two training facilities or to the much longer firing line at YTC. This would result in a larger area where deposition occurs, and thus more diffuse deposition over a larger area. In terms of usage, though, FL has a large resident military force on site, whereas training at YTC is completely due to visiting military units from other areas.

At YTC we collected a set of profile samples from the surface to a depth of 35 cm at a location 12 m behind the firing line (Table 3-7). The concentration from 0 to 7 cm at this position was only 1.14 mg/kg and yet the concentrations at 12 to 17 cm and 21 to 25 cm were 1.86 and 2.66 mg/kg, respectively. The NG breakdown products discussed above also were found in these subsurface samples. No profile samples were collected at FL range 59, though, because the soil profile contains a layer of small stones at about a 5-cm depth, and penetrating into this layer with hand tools is impossible.

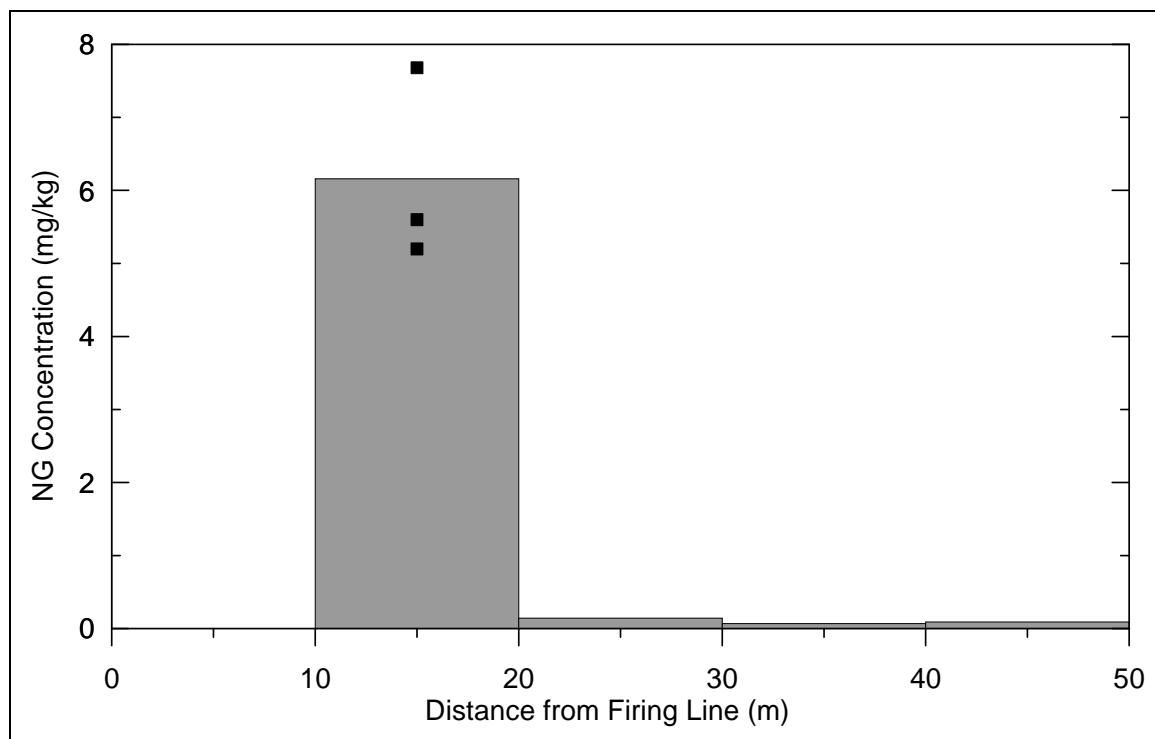
The apparent mobility of NG into the shallow soil profile was unexpected at YTC because of the low rainfall for this area. Downward penetration of NG at antitank rocket ranges has been found in other, more moist, locations. At CFB-Gagetown, NG concentrations in soil profile samples at 0 to 2 cm, 2 to 5 cm, and 5 to 10 cm near antitank targets were found to be 20.4, 15.0, and 43.6 mg/kg, respectively (Thiboutot et al. 2003). NG concentrations in soil profile samples at 10 m behind the firing line at Gagetown decreased from 20.0 mg/kg in the 0- to 5-cm depth to 5.79 mg/kg at the 27- to 35-cm depth (Thiboutot et al. 2004). Thus far, however, there have been no reports of NG in groundwater samples from antitank rocket range areas, or at any other range, although the number of locations where groundwater samples at ranges have been analyzed for NG is uncertain.

**Table 3-7. Concentrations of NG in soil samples from LAW and AT-4 rocket firing point areas at YTC range 7 and FL range 59. All samples were collected behind firing line.**

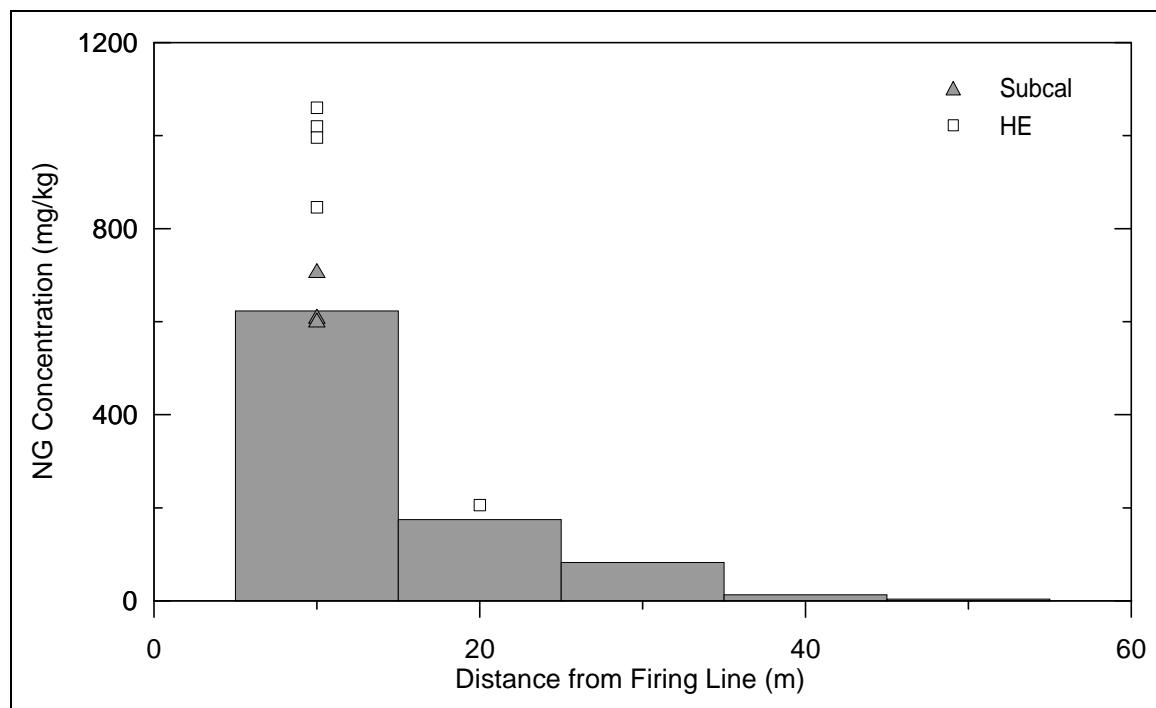
Sample number	Location	Core diameter (cm)	Depth (cm)	Increments	NG		
					Concentration (mg/kg)	Mean	% RSD
YTC range 7							
<i>Surface</i>							
53					7.00		
54					5.76	5.97	15.7
55					5.16		
56					5.60		
57					5.20	6.16	21.6
58					7.68		
59					6.94		
60					8.20	7.11	14.2
61					6.20		
62	20–30 m	3-cm	0–2.5	47	0.14		
63	30–40 m	3-cm	0–2.5	48	0.07	0.10	37.7
64	40–50 m	3-cm	0–2.5	44	0.09		
<i>Depth profile</i>							
65	12 m	scoop	25–30	Discrete	0.06		
66	12 m	scoop	21–25	Discrete	2.66		
67	12 m	scoop	17–21	Discrete	0.09		
68	12 m	scoop	12–17	Discrete	1.86		
69	12 m	scoop	7–12	Discrete	0.10		
70	12 m	scoop	0–7	Discrete	1.14		
FL range 59 Sub-cal area							
1					710		
2					612	623	9.85
3					604		
4					566		
5					581		
6					558	591	5.72
7					586		
8					638		
9	15–25 m	2-cm	0–2.5	25	175		
10	25–35 m	2-cm	0–2.5	25	82.4		
11	35–45 m	2-cm	0–2.5	25	13.0		
12	45–55 m	2-cm	0–2.5	25	3.36		
13					680		
14					616	660	12.9
15					575		
16					770		
17					728		
18					606	641	9.75
19					642		
20					587		

**Table 3-7 (cont'd). Concentrations of NG in soil samples from LAW and AT-4 rocket firing point areas at YTC range 7 and FL range 59. All samples were collected behind firing line.**

Sample number	Location	Core diameter (cm)	Depth (cm)	Increments	NG		
					Concentration (mg/kg)	Mean	% RSD
<b>FL range 59 Sub-cal area</b>							
21	5–15 m	4-cm	0–2.5	6	356	486	18.3
22					556		
23					506		
24					524		
25	5–15 m	4-cm	0–2.5	1	208	189	31.0
26					250		
27					190		
28					110		
<b>HE area</b>							
59	5–15 m	2-cm	0–2.5	25	1020	981	9.5
60					846		
61					996		
62					1060		
63	5–15 m	4-cm	0–2.5	25	1070	1010	13.9
64					808		
65					1130		
66					1020		
67	5–15 m	2-cm	0–2.5	100	760	818	8.6
68					758		
69					896		
70					859		
71	15–25 m	2-cm	0–2.5	25	206		
72	5–15 m	4-cm	0–2.5	6	1200	1120	21.3
73					1030		
74					840		
75					1400		
76	5–15 m	4-cm	0–2.5	1	167	223	23.3
77					232		
78					290		
79					204		



**Figure 3-22. Nitroglycerin concentration (mg/kg) with distance from firing point at Yakima Training Center range 7, where troops train with HE-filled M-72 LAW and AT-4 rockets. Histogram data are results for composite samples taken with 3-cm-diameter cores within each decision unit. Square symbols show the three field replicates for the decision unit between 10 m and 20 m.**



**Figure 3-23. Nitroglycerin concentration (mg/kg) with distance from firing point at Fort Lewis range 59, where troops train with sub-cal and HE-filled LAW and AT-4 rockets. Histogram data are results for composite samples taken with 2-cm-diameter cores within each decision unit in the sub-cal lanes. Triangle symbols show the three field replicates for the decision unit between 5 m and 15 m. Square symbols show results for the HE lanes.**

#### 40-mm Grenade Firing Areas

Two ranges where 40-mm grenades are fired were sampled at YTC. Range 8 is a dedicated 40-mm range. Range 26 is a firing area just outside of the central impact area and is used for firing many types of weapons systems. We sampled areas in front of and behind the firing line at range 8 and at two areas where we observed troops firing 40-mm grenades at range 26. Three types of propellant are used for launching 40-mm rifle grenades. The first is single-base M1 propellant, with 85% NC, 10% 2,4-DNT, and 5% dibutylphthalate, and 1% diphenylamine. The other two types are double-base propellants—M2 and M9. The M2 formulation has 77% NC, 19% NG, and small amounts of ethyl centralite, barium nitrate, potassium nitrate, and graphite. M9 propellant has 58% NC, 40% NG and small amounts of ethyl centralite, potassium nitrate, and graphite.

The only target analyte consistently detected at range 8 was NG. The mean concentration in the 0- to 10 -m area in front of and behind the firing line was

1.14 and 0.24 mg/kg, respectively (Table 3-8). The concentrations found for samples collected beyond 10 m either in front or behind the firing line were all less than 0.05 mg/kg, our analytical detection limit for NG. Thus it appears that the magnitude of NG deposition from 40-mm grenades is much smaller than found at antitank rocket ranges and is largely confined to the areas within 10 m of the firing line.

**Table 3-8. Concentrations of nitroglycerin in soil samples from 40-mm firing point areas.**

Sample number	Front/ behind <sup>1</sup>	Distance	Core diameter	Depth (cm)	Increments	NG									
						Concentration (mg/kg)	Mean (mg/kg)	% RSD							
<b>YTC range 26</b>															
<i>40-mm practice and HE area</i>															
1	Front	0–10 m	3-cm	0–2.5	37	3.16	2.81	13.6							
2						2.86									
3						2.40									
4		10–20 m	3-cm	0–2.5	43	1.41	1.72	16.2							
5						1.79									
6						1.95									
<i>Single illumination</i>															
7	Front	0–10 m	3-cm	0–2.5	30	0.28	0.24	28.9							
8						0.28									
9						0.16									
<b>YTC range 8</b>															
<i>Surface</i>															
10	Front	0–10 m	3-cm	0–2.5	50	1.05	0.91	13.7							
11						0.81									
12						0.87									
13	Front	10–20 m	3-cm	0–2.5	50	<0.05									
14	Front	40–50 m	3-cm	0–2.5	50	<0.05									
15	Behind	0–10 m	3-cm	0–2.5	50	0.33	0.27	37.9							
16						0.15									
17						0.32									
18	Behind	10–20 m	3-cm	0–2.5	50	<0.05									
19	Behind	20–30 m	3-cm	0–2.5	50	<0.05									
20	Behind	30–40 m	3-cm	0–2.5	50	<0.05									
25	Behind	0–10 m	4-cm	0–2.5	50	0.24	0.21	25.8							
26						0.15									
27						0.25									
28	Behind	0–10 m	2-cm	0–2.5	50	0.30	0.26	41.7							
29						0.14									
30						0.35									

<sup>1</sup> Location relative to firing line.

**Table 3-8 (cont'd). Concentrations of nitroglycerin in soil samples from 40-mm firing point areas.**

Sample number	Front/behind <sup>1</sup>	Distance	Core diameter	Depth (cm)	Increments	NG								
						Concentration (mg/kg)	Mean (mg/kg)	% RSD						
31	Behind	0–10 m	4.75-cm	0–2.5	50	0.25	0.21	25.8						
32						0.24								
33						0.15								
35	Front	0–10 m	2-cm	0–2.5	50	1.32	1.31	12.8						
36						1.48								
37						1.35								
38						1.08								
39	Front	0–10 m	3-cm	0–2.5	50	1.34	1.15	21.6						
40						1.28								
41						1.18								
42						0.79								
43	Front	0–10 m	4-cm	0–2.5	50	1.05	1.13	17.0						
44						1.01								
45						1.42								
46						1.05								
<b>YTC range 8</b>														
<i>Depth samples</i>														
34 <sup>2</sup>	Behind	0–10 m	4.75-cm	2.5–5.0	50	<0.05								
47	Front	2 m	scoop	23–28		0.09								
48	Front	2 m	scoop	19–23		0.16								
49	Front	2 m	scoop	12–19		0.12								
50	Front	2 m	scoop	9–12		<0.05								
51	Front	2 m	scoop	3–9		0.28								
52	Front	2 m	scoop	0–3		0.08								

<sup>1</sup> Location relative to firing line.

<sup>2</sup> Positioned beneath sample 31.

NG concentrations in the profile samples at range 8 were all low, the highest being 0.28 mg/kg between 3 and 9 cm below surface. NG was detected at 0.09 mg/kg in the soil segment from 23- to 28-cm depth, the deepest segment collected. Here again, it does appear that NG is being carried deeper into the soil profile at YTC than anticipated, although the concentrations are quite low at this range. NG breakdown products were also detected in these subsurface samples.

At range 26, NG was the only target analyte consistently detected, although a trace of RDX was detected in one sample. The mean concentration of NG in the 0- to 10-m and 10- to 20-m areas where the practice and HE-filled 40-mm grenades were fired were 2.81 and 1.72 mg/kg, respectively. The similar con-

centrations for both areas is in contrast to that found at range 8. Thus, it is likely that at least a portion of the NG found at this location on range 26 was due to the firing of other types of weapons.

The second area sampled at range 26 was hundreds of meters from the fence line in an area along an access road. It did not appear to be a position typically used for firing activities, but was apparently randomly selected to fire 40-mm illumination rounds. The mean NG concentration found for the surface soil (0- to 2.5-cm depth) in this 10-m × 10-m area was 0.24 mg/kg. Here again, deposition of NG from firing of 40-mm grenades appears to be quite small.

#### *Small Arms Ranges (YTC Ranges 15 and 4) (FL Ranges 93 and 93Z)*

Lead accumulation and leaching at target areas on small arms ranges has been studied, but very little research has been conducted on the deposition of propellant residues at small arms firing points. This study sampled five ranges where small arms are fired at YTC and FL. At YTC, soil samples were collected at ranges 15 and 4. At range 15, vehicle-mounted troops fire small arms against simulated enemy attacks along a traveled route. The first two areas sampled were along the traveled route where simulated enemy attacks occur and troops return fire with 5.56- and 7.62-mm rounds. No target analytes were detected in soil samples from these areas.

The third area sampled at range 15 was in front of a gravel pad where all troops entering range 15 conduct their initial firing activity. NG was the only target analyte detected in these samples (Table 3-9). The mean NG concentration in the area from 0 to 10 m from the gravel pad was 1.68 mg/kg. In the areas 10–20 m, 20–30 m, 30–40 m, and 40–50 m in front of the pad, NG concentrations were 0.28, 0.07, 0.14, and 0.07 mg/kg, respectively (Fig. 3-24). Thus the deposition of NG at this range is small and the concentration rapidly decreases to barely above the analytical detection limit at a distance of 50 m from the firing area.

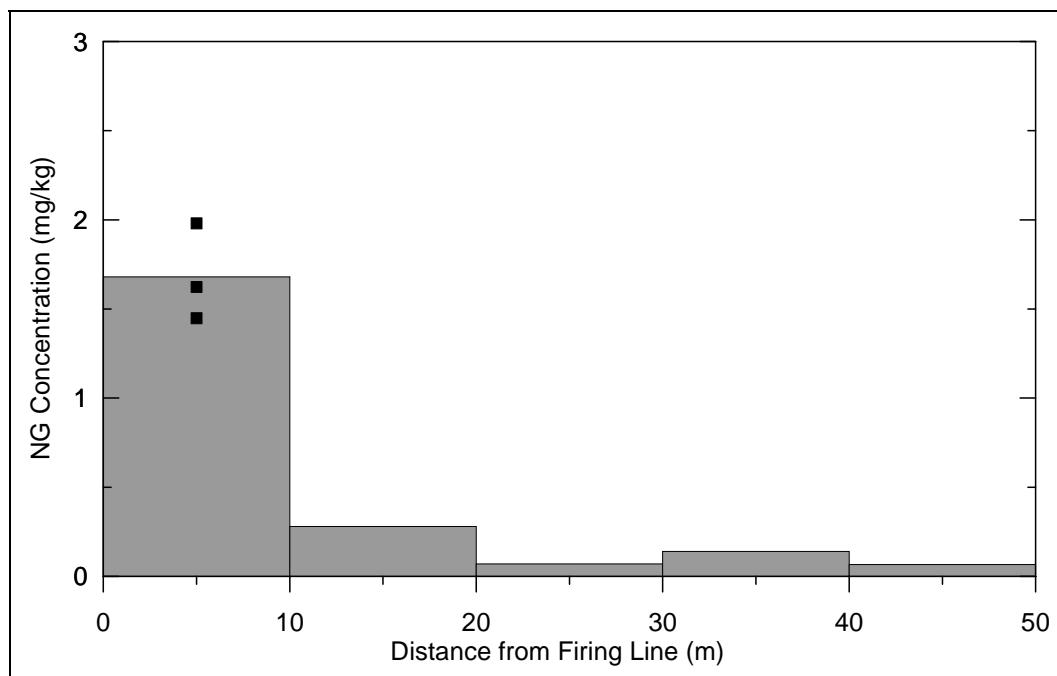
Range 4 at YTC is used for dismounted firing of small arms, mainly 5.56-mm and pistols. Only one sample was collected at a distance from 0 to 10 m from the firing area. The NG concentration in this sample was 85.0 mg/kg (Table 3-9).

At Fort Lewis, we collected soil samples at ranges 93 and 93Z. Range 93Z is used for practice firing of machine guns. NG was the target analyte detected at highest concentration on this range. The mean NG concentration found for the area from 0 to 10 m from the firing area was 8.60 mg/kg (Table 3-9). In the more distant samples, 10 to 20 m and 20 to 30 m, NG concentrations were 2.14 and 1.21 mg/kg, respectively. Minor amounts of 2,4-DNT were also detected at this range; the concentration in the area from 0 to 10 m from the firing point was only

0.074 mg/kg and the concentrations in the areas from 10 to 20 m and 20 to 30 m were both below the analytical detection limit of 0.05 mg/kg.

**Table 3-9. Concentrations of NG and 2,4-DNT in soil samples from small arms firing point areas at YTC range 15 and range 4, and FL range 93 and 93Z.**

Sample number	Location	Distance	Core diam.	Depth (cm)	Increments	NG			2,4-DNT							
						Conc. (mg/kg)	Mean (mg/kg)	% RSD	Conc. (mg/kg)	Mean (mg/kg)	% RSD					
<b>YTC range 15</b>																
<i>Surface</i>																
73	Firing point	0–10 m	3-cm	0–2.5	36	1.98	1.68	16.1								
74	Firing point					1.45										
75	Firing point					1.62										
76	Firing point	10–20 m	3-cm	0–2.5	36	0.28										
77	Firing point	20–30 m	3-cm	0–2.5	36	0.07										
78	Firing point	30–40 m	3-cm	0–2.5	36	0.14										
79	Firing point	40–50 m	3-cm	0–2.5	36	0.07										
<i>Depth profile</i>																
80		2 m	scoop	9–14		0.25										
81		2 m	scoop	5–9		0.31										
82		2 m	scoop	0–5		2.06										
<b>YTC range 4</b>																
83	Firing point	0–10 m	3-cm	0–2.5	36	85.0										
<b>FL range 93Z</b>																
39	Firing point	0–5 m	2-cm	0–2.5	35	10.7	8.60	21.7	0.094	0.07	23.7					
40	Firing point					7.29			0.069							
41	Firing point					7.78			0.060							
42	Firing point	5–10 m	2-cm	0–2.5	35	2.14			<d							
43	Firing point	10–15 m	2-cm	0–2.5	35	1.21			<d							
<b>FL range 93</b>																
44	FP Lane 2	0–5 m	2-cm	0–2.5	25	398			<d							
45	FP Lane 2	5–10 m	2-cm	0–2.5	25	275			3.0							
46	FP Lane 3	0–5 m	2-cm	0–2.5	25	522	504	7.2	<d							
47						528			<d							
48						462			<d							
49	FP Lane 3	5–10 m	2-cm	0–2.5	25	322	276	16.9	3.6							
50						229										
51						276										
52	FP Lane 4	0–5 m	2-cm	0–2.5	25	336			4.0							
53	FP Lane 4	5–10 m	2-cm	0–2.5	25	206			2.0							

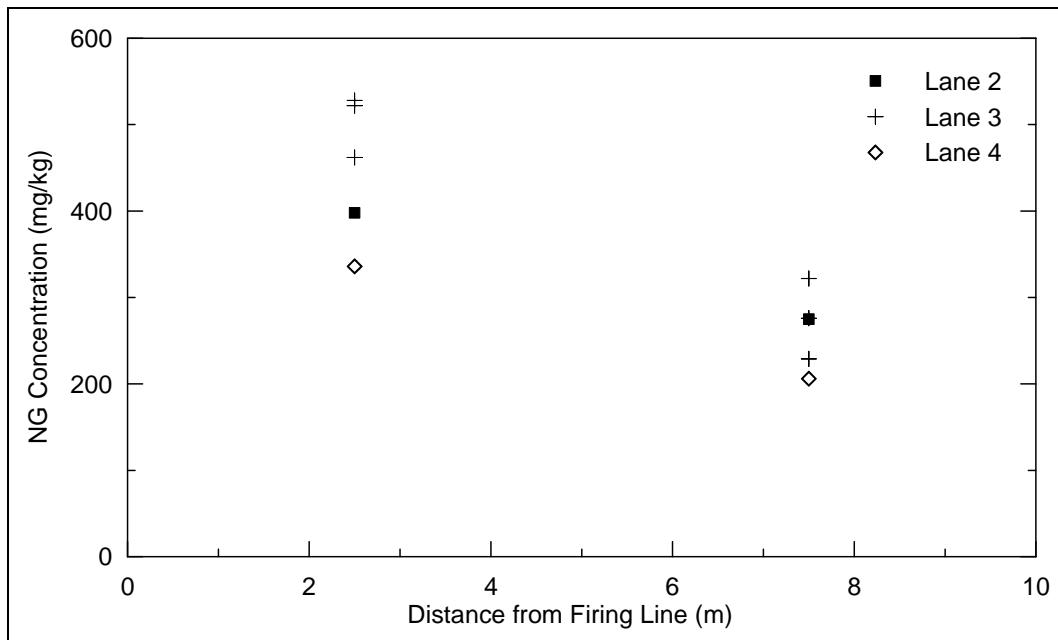


**Figure 3-24.** Nitroglycerin concentration (mg/kg) with distance from firing point at YTC range 15, where troops train with small arms weapons. Histogram displays results for composite samples taken with 3-cm-diameter cores within each decision unit. Square symbols show the three field replicates for the decision unit between 0 m and 10 m.

Range 93 is used for target practice with M16 rifles using 5.56-mm ammunition. NG and 2,4-DNT were detected in soil samples from this range, but concentrations of NG were two orders of magnitude higher than 2,4-DNT (Table 3-9). The NG concentrations in the 0- to 5-m surface soil samples were 398, 522, and 336 mg/kg for the three firing lanes, respectively. Similarly, the NG concentrations in the 5- to 10-m areas were 275, 276, and 206 mg/kg (Fig. 3-25).

The only other results for propellant compounds at small arms ranges that we are aware of is work conducted by our Canadian colleagues at CFB-Petawawa (Brochu et al. in press). At two rifle ranges, they report that only 2,4-DNT was detected with a maximum concentration of 2.3 mg/kg in surface soils. They indicated that the 5.56-mm ammunition fired at these ranges is double base that contains 2,4-DNT. At a pistol range, the Canadians detected only 2,4-DNT as well with a maximum concentration of 9.6 mg/kg at a distance of 5 m from the firing line. Although we also detected low concentrations of 2,4-DNT at several of the small arms ranges that we sampled, NG was found at higher concentrations in all cases. The reason for the differences observed is uncertain. Additional

sampling has been conducted at these ranges at Petawawa and NG has now been detected (Brochu, personal communication).



**Figure 3-25. Nitroglycerin concentration (mg/kg) with distance from firing point at Fort Lewis range 93, where troops train with small arms weapons. The results for lanes 2, 3, and 4 are shown with separate symbols.**

#### Artillery/Mortar Ranges

Three artillery/mortar firing positions were sampled. The first was at the Multi-Purpose Range Complex (MPRC) at YTC, the second was a 155-mm firing position at FL, and the third was an artillery firing position at FB. At the MPRC, 81-mm mortars had been fired over the previous night prior to our sampling at a firing position that did not appear to be used routinely. The exact firing position was located from the imprint of the base plate on the soil. Duplicate multi-increment surface soil samples were collected from 0 to 10 m and 10 to 20 m downrange of the firing position. A trace of NG was detected in two of the four samples, but the concentrations were all below a detection limit of 0.05 mg/kg (Table 3-10).

At firing point FP3409 at FL, surface soil samples were collected in areas from 15 m to 45 m downrange from the muzzle of a 155-mm howitzer the morning after an all-day-and-night firing event. Tens of rounds had been fired from this howitzer prior to sample collection. No target analytes, including NG

and 2,4-DNT, were detected; detection limits for NG and 2,4-DNT were 0.02 mg/kg. These results are consistent with the very low deposition of 2,4-DNT found when 155-mm howitzers were fired at a snow-covered range (M.R. Walsh et al. 2005). Walsh estimated that an average of only  $45 \mu\text{g}/\text{m}^2$  of 2,4-DNT was deposited per round fired in the 30-m  $\times$  30-m area downrange of the muzzle. Even if 100 rounds were fired, only 4.5 mg of 2,4-DNT would have been deposited over the 30-m  $\times$  30-m area and the amount present in these surface soil samples would be much too low to be detectable (only about 5 ng).

**Table 3-10. Concentrations of nitroglycerin in soil samples from mortar and artillery firing point areas at YTC-MPRC, FL-FP3409, and FB-artillery point 4.**

Sample number	Distance	Core diameter	Depth (cm)	Increments	NG
					Concentration (mg/kg)
<b>YTC-MPRC</b>					
21	0–10 m	2 cm	0–2.5	30	trace (<d)
22	0–10 m	2 cm	0–2.5	30	<d
23	10–20 m	2 cm	0–2.5	30	<d
24	10–20 m	2 cm	0–2.5	30	trace (<d)
<b>FL-FP3409 [155-mm firing point]</b>					
54	15–25 m	2 cm	0–2.5	30	<d
55	15–25 m	2 cm	0–2.5	30	<d
56	15–25 m	2 cm	0–2.5	30	<d
57	25–35 m	2 cm	0–2.5	30	<d
58	35–45 m	2 cm	0–2.5	30	<d
<b>FB-artillery point 4</b>					
B1	0–100 m <sup>1</sup>	scoops	0–5	100	2.22
B2	0–100 m	scoops	0–5	100	2.28
B3	0–100 m	scoops	0–5	100	2.68

<sup>1</sup> Area sampled was a 100 m  $\times$  100 m grid at firing point.

At FB, triplicate multi-increment surface soil samples were collected in a 100-m  $\times$  100-m firing artillery/mortar position at firing point 4. The mean NG concentration was 2.39 mg/kg and the % RSD was 10.5% (Table 3-10). 2,4-DNT was not detected in these samples. Whether the NG residues were deposited from artillery or mortar is uncertain.

### *Urban Breaching Range*

Results from the analysis of samples from urban breaching range 62 at FL are presented in Table 3-11. Because the troops present when we sampled the range had just used det cord prior to our sampling, we expected the major residue at this range would be PETN, the explosive used in det cord. PETN was detected in nine of the ten soil samples with concentrations generally below 1 mg/kg. However, concentrations of RDX and HMX were much higher than that of PETN. In room G, the RDX and HMX concentrations averaged 50.0 and 11.7 mg/kg, respectively. Very low concentrations (< 0.2 mg/kg) of NG and TNT also were detected in most of these soil samples. Clearly, det cord is not the only explosive used at this range. From the magnitude of the RDX concentrations, it appears that training with C4 also has taken place here in the past.

**Table 3-11. Concentrations of energetic compounds at FL urban demolition range 62.**

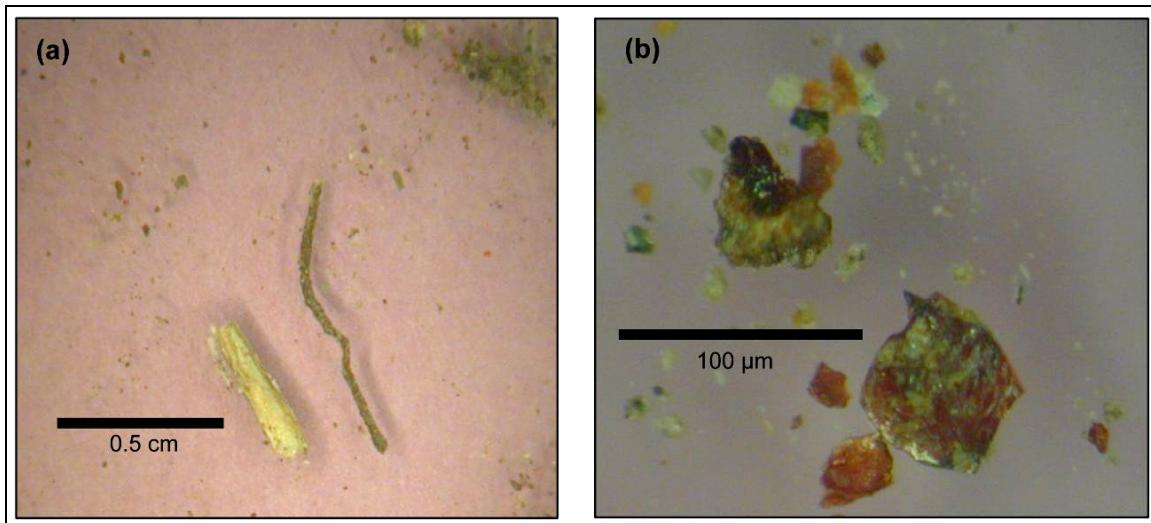
<b>Spl. no.</b>	<b>Area*</b>	<b>Concentration (mg/kg)</b>											
		<b>HMX</b>	<b>RDX</b>	<b>TNB</b>	<b>DNB</b>	<b>TNT</b>	<b>Tetryl</b>	<b>NG</b>	<b>2ADNT</b>	<b>4ADNT</b>	<b>2,4-DNT</b>	<b>2,6-DNT</b>	<b>PETN</b>
29	A	0.11	0.36	<d	<d	0.01	<d	0.12	<d	<d	0.39	<d	0.08
30	B	0.17	0.93	<d	<d	0.01	<d	<d	<d	<d	<d	<d	0.93
31	C	0.32	1.65	<d	<d	<d	<d	<d	<d	<d	<d	<d	0.18
32	D	0.85	5.50	<d	<d	0.01	<d	0.02	<d	<d	<d	<d	<d
33	E	0.54	2.84	<d	<d	0.02	<d	0.07	<d	<d	<d	<d	1.30
34	F	1.49	7.62	<d	<d	0.02	<d	0.17	<d	<d	<d	<d	0.83
35	G	11.4	47.1	0.07	<d	0.02	<d	<d	<d	<d	<d	<d	0.65
36	G	11.5	49.2	0.07	<d	0.03	<d	0.06	<d	<d	<d	<d	0.15
37	G	12.3	53.8	0.08	<d	0.02	<d	0.06	<d	<d	<d	<d	0.16
38	H	2.8	13.3	0.02	<d	0.03	<d	0.02	<d	<d	<d	<d	0.11

\* See Figure 3-16.

### *Microscopic Analysis of Propellant Residues*

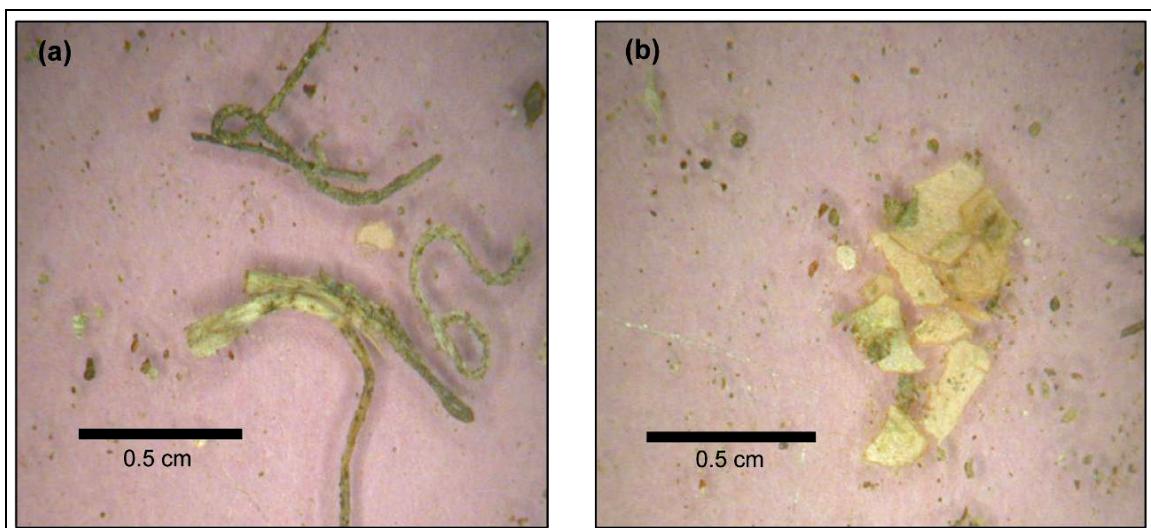
#### **Yakima Training Center**

Residues were collected during the firing of seven LAW rockets and two AT-4 rockets on range 7 at YTC. Two particle types deposited from the LAW rockets were suspected of coming from the propellant—fibers and red-colored particles (Fig. 3-26). We extracted both types of particles with acetonitrile and the extracts were analyzed by RP-HPLC-UV. The fibers (Fig. 3-26a) contained nitroglycerin (NG) and RDX. The red particles (Fig. 3-26b) contained no NG but did contain small amounts of RDX and TNT.



**Figure 3-26. Microphotographs of particles collected after firing of HE-filled M-72 LAW rockets at Yakima Training Center range 7. The particles include (a) fibers containing NG and RDX and (b) red particles containing RDX and TNT.**

The AT-4 residues also had two types of solids, possibly from the propellant. One was labeled AT-4 fibers (Fig. 3-27a) and the other white platelets (Fig. 3-27b). The AT-4 fibers had substantial NG. The AT-4 white platelets had a large amount of NG. We suspected that the white platelets were nitrocellulose, because they became translucent when the acetonitrile was added, so the presence of NG was anticipated.



**Figure 3-27. Microphotographs of particles collected after firing of HE-filled AT-4 rockets at Yakima Training Center range 7. The particles include (a) fibers containing substantial NG and (b) white platelets that may be NC.**

### Fort Lewis

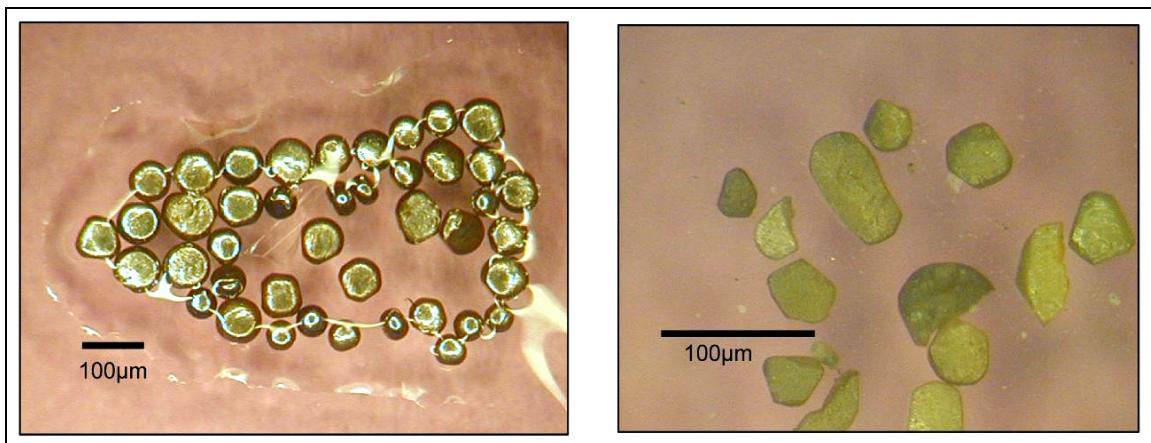
The residues deposited from repeated firing of a single 155-mm howitzer at Firing Point 3409 using green bag single-base (NC) M3A1 propelling charge were similar to those found by M.R. Walsh et al. (2005): mainly round clear particles that are not propellants and which dissolve in acetone (stabilizer or binder component) (Fig. 3-28). Scanning electron images and X-ray analyses of these grains show that they consist of different layers, like an onion, and contain traces of potassium and sulfur.



**Figure 3-28. Microphotograph of round, clear particles collected after live firing of a 155-mm howitzer with M1 single-base propellant at Fort Lewis firing point 3409.**

Residues from 20 rounds of an M16 were also collected. The M16 rifle utilizes several types of rounds, but most have double-base propellants with NC:NG percentages such as 80:11, 73:19, and 72:17; additional components include dibutyl phthalate, diphenylamine, ethyl centralite, sodium sulfate, calcium carbonate, and graphite. We found rounded, flattened particles that

are similar to unused propellant grains removed from small arms cartridges (Fig. 3-29). The particles are pale green in color and translucent when very thin.



**Figure 3-29. Microphotographs of propellant grains collected from unused cartridges for 5.56-mm M16 rifles.**

This information is important when trying to develop the appropriate sample collection and sample processing steps, as has been shown by Walsh et al. (in press) for propellant residues in soil from 105-mm howitzers firing M1 propellant.

#### *Nitrocellulose Concentrations*

Two small batches of soil samples from YTC and FL were analyzed for nitrocellulose (NC). The purpose was to determine whether the NC levels accumulating at firing points were predictable relative to NG. Previous investigations have ignored NC because of the lack of a reliable method of analysis for NC in soil, and the lack of any identified environmental risk associated with this compound. The first set was analyzed at the ERDC laboratory in Omaha and the quality assurance results were acceptable for this set of samples. Because this laboratory was closed prior to the second set of analyses, the second set was analyzed in a commercial laboratory. The quality assurance results for this set of samples were much poorer than for the original set. Generally, recovery for fortified samples in the second set of samples was low. All results are presented in Table 3-12 along with concentrations of NG obtained at ERDC-CRREL.

Overall, the NC results mimic those for NG; where NG values are high, the NC values are high as well. Likewise, when NG values are less than 20 mg/kg, NC values are non-detectable (<20 mg/kg). The average ratio (NC/NG) for all

samples analyzed is 4.6, with the ratios ranging from 1.6 to 7.1. The average ratio for the first batch is 4.9 and that for the second batch is 4.3, perhaps a result of the low recovery found for batch 2.

**Table 3-12. Comparisons of nitrocellulose (NC) and nitroglycerin (NG) concentrations in a variety of firing point samples.**

Site	Range/Area	Distance (m)	Sample number	Concentration (mg/kg)		NC/NG ratio
				NG	NC	
<b>FL</b>	LAW & AT-4 Sub-cal	5–15	F1	710	4640	6.5
		15–25	F9	175	583	3.3
		25–35	F10	82.4	439	5.3
		35–45	F11	13	<20	—
		45–55	F12	3.4	<20	—
	LAW & AT-4 HE	5–15	F59	1020	3970	3.9
		5–15	F62	1060	5870	5.5
		15–25	F71	206	483	2.3
	Machine gun	0–5	F39	10.7	22	2.1
	Small arms	0–5	F44	398	1680	4.2
		5–10	F45	275	871	3.2
		0–5	F46	522	3560	6.8
		5–10	F49	322	2006	6.2
<b>YTC</b>	40-mm grenades	0–10	Y36	1.48	<20	—
	LAW & AT-4 rockets	10–20	Y53	7.00	583	3.0
		10–20	Y54	5.80	41.0	7.1
		10–20	Y60	8.20	54.5	6.7
		20–30	Y62	0.14	<20	—
		30–40	Y63	0.07	<20	—
		40–50	Y64	0.09	<20	—
	40-mm illumination	0–10	Y83	85.0	449	5.3
		0–10	Y83 (dup)	85.0	133	1.6
					<b>Mean</b>	<b>4.6</b>
					<b>Standard deviation</b>	<b>1.85</b>

The results are from a variety of ranges, including an antitank rocket range, several small arms ranges, and a 40-mm grenade range. There are insufficient data to compare the ratio for various types of ranges.

The ratio of NC/NG for the various propellants used on small arms ranges and antitank rocket ranges varies substantially. For example, three different types of propellant are used with 5.56-mm ammunition. WC814 has a NC/NG ratio of 3.9, WC844 has a ratio of 7.3, and WCR845 has a ratio of 4.1. The ratio for the propellant used in 66-mm LAW rockets is 1.5, but the ratio for the AT-4 rockets is unavailable due to the proprietary nature of that formulation.

The ratio of NC/NG for soils at firing points should increase over time, as the NG is extracted from the NC matrix by rainfall. NC is a polymeric material and is insoluble in water.

## Conclusions

Of the ranges that we sampled, the highest concentrations of propellant-related residues were detected at antitank rocket ranges and small arms ranges. At antitank rocket ranges, NG concentrations in surface soils can be in the thousands of mg/kg and NG residues have been detected at distances as great as 50 m behind the firing line. For small arms ranges, NG can be in the hundreds of mg/kg just in front of the firing line, but the area of deposition has not been well defined.

Sampling at a 155-mm howitzer firing point indicates that very little energetic residue is deposited from this firing activity. These results confirm the findings by Walsh et al. (2006) from firing activities on snow-covered ranges, and earlier attempts to detect residues from 155-mm firing activities in surface soils at Yakima Training Center and Camp Guernsey (Pennington et al. 2002), and at Fort Bliss (USACHPPM 2002).

NG residues were detected at 40-mm grenade firing points. Deposition appears to be limited to areas from 0 to 10 m in front of and behind the firing line, and mean concentrations were always less than 3 mg/kg in surface soils.

Limited collection of depth profile samples indicates that NG is leaching into shallow subsurface soils. Transformation products of NG degradation also were found in many subsurface samples. Although there have been no reports of NG or its transformation products in water samples from groundwater wells at training ranges, collection of additional soil profile samples and water samples from lysimeters emplaced at firing point areas is needed to define the ultimate fate of NG at firing point areas.

Propellant residues are deposited at firing point areas as discrete particles of burnt and unburnt fibers and platelets of propellant composed of polymeric NC with NG or 2,4-DNT imbibed within the NC matrix. The collection of representative samples to reliably estimate mean residue concentrations can be a difficult

challenge. Sampling experiments at antitank firing point areas indicate that multi-increment surface soil samples collected using a systematic-random sampling design provide reproducible results for energetic propellant residues. Although in some cases as few as six increments have provided RSDs for sample replicates less than 30%, we recommend that samples be constructed with between 30 and 100 increments and that samples have a mass of at least 300 grams.

Because of the presence of a fairly small number of individual fibers and small pieces of propellant in soil samples from firing points, it has been difficult to obtain representative subsamples from firing point soils. The sample processing and subsampling protocols developed by Walsh et al. (2004, *in press*) provide reliable subsamples from soil samples containing propellant residues. These protocols require that samples be air-dried, passed through a 10-mesh (2-mm) sieve to remove oversize material, and adequately pulverized using a mechanical grinder.

Samples collected at an urban demolition range indicated that RDX and low concentrations of PETN were present in soils. Most of the demolition at this range uses det cord, which contains PETN. The RDX detected at this range is probably due to the occasional use of C4 demolition explosive here.

## References

**Brochu, S., E. Diaz, S. Thiboutot, G. Ampleman, A. Marois, A. Gagnon, A.D. Hewitt, S.R. Bigl, M.E. Walsh, K. Bjella, C. Ramsey, S. Taylor, N. Van Ham, A. Creemers, M. Ahberg, H. Wingfors, R.M. Karlsson, and U. Qvarfort** (2006) Assessment of 100 years of military training in Canadian Force Base Petawawa. Chapter 3 in Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 6. ERDC TR-06-12. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Hewitt, A.D., T.F. Jenkins, T.A. Ranney, D. Lambert, and N. Perron** (2004) Characterization of energetic residues at military firing ranges: Schofield Barracks and Pohakuloa Training Area. In Distribution and Fate of Energetics on DoD Test and Training Ranges; Interim Report 4. ERDC TR-04-4. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Jenkins, T.F., and S.M. Golden** (1993) Development of an improved confirmation separation suitable for use with EPA SW846 Method 8330. CRREL Special Report 93-11. Hanover, NH: U.S. Army Cold Regions Research and Engineering Laboratory.

**Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and Major E. Wahlgren** (2001) Characterization of explosives contamination at military firing ranges. ERDC/CRREL TR-01-05. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

**Jenkins, T.F., T.A. Ranney, A.D. Hewitt, M.E. Walsh, and K.L. Bjella** (2004) Representative sampling for energetic compounds at an antitank firing range. ERDC/CRREL TR-04-7. Hanover, NH: U.S. Army Research and Development Center, Cold Regions Research and Engineering Laboratory.

**Jenkins, T.F., A.D. Hewitt, M.E. Walsh, T.A. Ranney, C.A. Ramsey, C.L. Grant, and K.L. Bjella** (2005) Representative sampling for energetic compounds at military training ranges, *Journal of Environmental Forensics* 6: 45–55.

**Jenkins, T.F., A.D. Hewitt, C.L. Grant, S. Thiboutot, G. Ampleman, M.E. Walsh, T.A. Ranney, C.A. Ramsey, A. Palazzo, and J.C. Pennington** (2006) Identity and distribution of residues of energetic compounds at Army live-fire training ranges. *Chemosphere* 63: 1280–1290.

**Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, D. Lambert, J. Clausen and J.J. Delfino** (2002) Distribution and fate of energetics on DoD test and training ranges: Interim Report 2. ERDC TR 02-8. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lewis, J.E. DeLaney, J. Clausen, A.D. Hewitt, M.A. Hollander, C.A. Hayes, J.A. Stark, A. Marois, S. Brochu, H.Q. Dinh, D. Lambert, A. Gagnon, M. Bouchard, R. Martel, P. Brousseau, N.M. Perron, R. Lefebvre, W. Davis, T.A. Ranney, C. Gauthier, S. Taylor, and J. Ballard** (2003) Distribution and fate of energetics on DoD test and training ranges, Interim Report 3. ERDC-TR-03-2. Vicksburg, MS: U.S. Army Engineer Research and Development Center.

**Pitard, F.** (2000) *Pierre Gy's Sampling Theory and Sampling Practice, 2nd Edition*. Boca Raton, Florida: CRC Press.

**Taylor, S., A. Hewitt, J. Lever, C. Hayes, L. Perovich, P. Thorne, and C. Daglian** (2004) TNT particle size distributions from detonated 155-mm howitzer rounds. *Chemosphere* 55: 357–367.

**Thiboutot, S., G. Ampleman, A. Hamel, J.M. Ballard, R. Martel, R. Lefebvre, and S. Downe** (2003) Environmental conditions of ground and surface water prevailing in the training area at CFB Gagetown, New Brunswick. DRDC Valcartier TR 2003-016. Québec, Quebec: Defence Research and Development Canada–Valcartier.

**Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T. Jenkins, M. Walsh, K. Bjella, C. Ramsey, and T.A. Ranney** (2004) Environmental conditions of surface soils, CFB Gagetown Training Area: Delineation of the presence of munitions-related residues (Phase III, Final Report). DRDC Valcartier TR 2004-205. Québec, Quebec: Defence Research and Development Canada–Valcartier.

**USACHPPM** (2004). Geohydrologic Study No. 38-EH-6807-02, Training range site characterization and risk screening, regional range study, Dona Ana Range, Fort Bliss, Texas, May 2002. Aberdeen Proving Ground, MD: U.S. Army Center for Health Promotion and Preventive Medicine.

**USACHPPM** (in press) Project No. 38-EH-00M2-04, Training range site characterization and risk assessment, regional range study, Redleg Impact Area, Fort Polk, Louisiana, March 2005. Aberdeen Proving Ground, MD: U.S. Army Center for Health Promotion and Preventive Medicine.

**U.S. Environmental Protection Agency** (1994) SW846 Method 8330. Nitroaromatics and nitroamines by HPLC. USEPA Office of Solid Waste standard methods of analysis test methods for evaluating solid wastes, physical and chemical methods. Update II (<http://www.epa.gov/sw-846/pdfs/8330.pdf>).

**U.S. EPA** (1999) Method 300.1: Determination of inorganic anions in drinking water by ion chromatography. Cincinnati, OH: U.S. Environmental Protection Agency National Exposure Research Laboratory. <http://www.epa.gov/safewater/methods/pdfs/met300.pdf>.

**Walsh, M.E., C.M. Collins, T.F. Jenkins, A.D. Hewitt, J. Stark, and K. Myers** (2003) Sampling for explosives residues at Fort Greely. *Soil and Sediment Contamination* 12: 631–645

**Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T.S. Douglas, N. Perron, D. Lambert, R. Bailey, and K. Myers** (2004) Range characterization studies at Donnelly Training Area, Alaska: 2001 and 2002. ERDC/CRREL TR-04-3. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

**Walsh, M.E., C.A. Ramsey, C.M. Collins, A.D. Hewitt, M.R. Walsh, K.L. Bjella, D.J. Lambert, and N.M. Perron** (2005) Collection methods and laboratory processing of samples from Donnelly Training Area firing points, Alaska, 2003. ERDC/CRREL TR-05-6. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

**Walsh, M.E., C.A. Ramsey, S. Taylor, A.D. Hewitt, K. Bjella, and C.M. Collins** (in press) Subsampling variance for 2,4-DNT in firing point soils. *Soil and Sediment Contamination*.

**Walsh, M.R.** (2004) Field sampling tools for explosives residues developed at CRREL. Technical Note ERDC/CRREL TN-04-1. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

**Walsh, M.R., S. Taylor, M.E. Walsh, S. Bigl, K. Bjella, T. Douglas, A. Gelvin, D. Lambert, N. Perron, and S. Saari** (2005) Residues from live fire detonations of 155-mm howitzer rounds. ERDC/CRREL TR-05-14. Hanover, NH: U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory.

## **4 Assessment of Gun Propellant Residues Dispersed by LG1 Mark II and C3 105-mm Howitzers from Static Artillery Firings**

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### **Introduction**

Military training ranges in Canadian Forces Bases are essential to prepare our troops for potential wars and peace missions. On the other hand, the growing environmental awareness of the Department of National Defence (DND) and of the population in general mandates that our Department evaluate the impact of training on the environment. During the last 10 years, methods for measuring the contamination by munitions residues have been developed (Ref. 1). A protocol describing different methods of sampling and the analytical chemistry was recently updated in collaboration with the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) and is now available under the auspices of the Technical Cooperation Program (TTCP) by the member nations (Canada, the U.S.A., the U.K., Australia, and New Zealand) in a key technical area (KTA 4-28) (Ref. 2). Testing and training ranges are key elements in maintaining the capability, readiness, and interoperability of the Armed Forces. On military training ranges, munitions-related constituents can be released into the environment from breaches in the casings of unexploded ordnance (UXO) or partially exploded ordnance (low-order detonations); from poor disposal practices, such as unconfined burning operations; from blow-in-place operations; and from live-fire operations. Many papers have been written in recent years concerning the characterization, analysis, fate, and transport of munitions-related residues in various types of sites (Ref. 1, 3–25).

Recently, awareness has increased regarding the fact that energetic residues and heavy metals associated with munitions can be released in the environment during training activities and over time potentially contaminate the groundwater. Moreover, requirements have emerged related to the identification, quantification, and elimination of energetic contaminants dispersed by munitions or present in explosives dumps, trials or destruction fields, firing areas, and production sites (Ref. 1–5, 8, 9, 11–14, 28, 34–41). Many Canadian Forces sites used as impact

areas, training ranges, and demolition and open burning/open detonation (OB/OD) ranges that were used to destroy out-of-specification materials were suspected of being contaminated with energetic constituents (Ref. 3, 4, 8, 9, 13, 14, 22, 28, 34, 35, 37, 41). For instance, munitions training and testing exercises were suspended at the Massachusetts Military Reservation following the discovery of low concentrations of hexogen (RDX) in the groundwater beneath the main training area (Environmental Protection Agency [EPA] Order #2). The Strategic Environmental Research and Development Program (SERDP) funded several studies directed at the assessment of source terms, pathways of biodegradation, and fate of munitions residues on military training facilities. In Canada, the Director Land Environment (DLE), which is part of the Department of National Defence (DND), tasked Defense Research and Development Canada (DRDC)–Valcartier to perform a research program for the environmental characterization of their main training areas.

Training range characterization efforts focused on target areas where explosives residues were thought to be present. Recently, however, firing positions were found to be contaminated with propellant residues such as nitroglycerin (NG) and 2,4-dinitrotoluene (DNT). These constituents are embedded in nitrocellulose (NC) fibers that are deposited in front of and around the guns (Ref. 26–29). NC is also a major ingredient in propellant formulations, but was not assayed for because it is not considered toxic. A preliminary study was conducted in 2003 to evaluate the deposition of the gun residues from artillery gun firing at Canadian Forces Base (CFB) Valcartier by placing aluminum witness plates at specified distances in front of the muzzle of the gun (Ref. 30). At CRREL, artillery activity residues were evaluated using snow cover to characterize the plume of deposition of the propellant residues (Ref. 25, 31). Both studies demonstrated that the gun expels propellant residues during firings. Nitrocellulose fibers containing 2,4-DNT were collected and analyzed. In 2006, Walsh et al. studied the contamination of mortar firing positions (Ref. 32). NG was found at significant concentrations, especially with the 81-mm mortars rounds.

In May 2005, the Fifth Royal Canadian Horse Artillery from CFB Valcartier held a major artillery exercise at CFB Gagetown. Our team seized this opportunity to study the dispersion of particles from artillery firing activities and assess the energetic materials residues. The objective was to evaluate the quantity of residues expelled after firing with two different guns and to understand the effect of the internal ballistics by varying the propellant charges. The two guns, the LG1 Mark II and the C3 105-mm howitzers, are depicted in Figure 4-1. The residues collected at the firing positions came from the single-base propellant M1,

composed of 85% NC, 10% 2,4-DNT, and 5% dibutylphthalate. Other ingredients present at less than 1% are diphenylamine and potassium sulphate (Ref. 33).



a. C3 105-mm howitzer.



b. LG1 Mark II 105-mm howitzer.

Figure 4-1. Two types of guns used by the Canadian Army.

In this trial, witness plates were used to collect gun propellant residues and to evaluate our sampling methods. The area covered by the plates was larger than the surface studied in 2003 (Ref. 30). Our objective was to evaluate the entire plume of contamination. Another objective was to measure the contamination of the soil in front of the muzzle of the guns by sampling the soil before and after the exercise. We also evaluated which gun, the LG1 Mark II or the C3, produced more residues. We also determined the influence that the number of bags of propellant had on the quantity of residues.

## **Experimental Methods**

Estimates of the amount of residues deposited by static live-firing of the LG1 Mark II 105-mm howitzer and the C3 105-mm howitzer were made by measuring soil samples and samples collected from aluminum witness plates. The following section describes the sampling patterns and extraction and analytical methods for soils and residues collected on aluminum plates.

### *Soil Sampling*

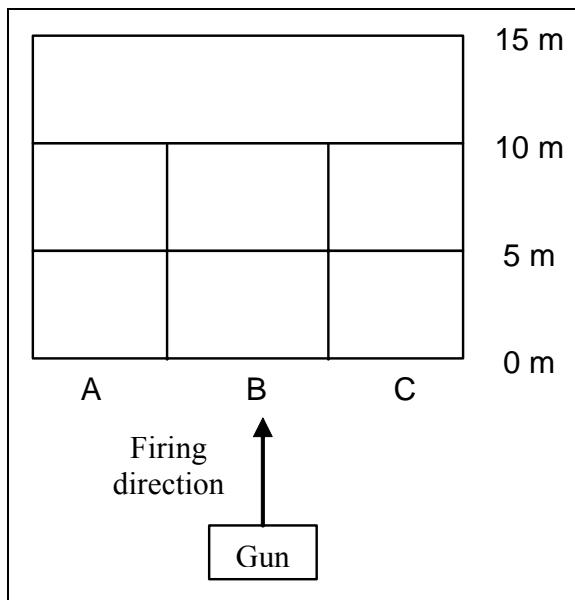
#### **Background samples**

Background soil samples were taken before the firings to estimate the concentration of energetic materials already present in the soil. Since the ranges were used in the past for training, differentiation of current and past residues would have been impossible without background samples. Therefore, before the guns were fired, soil samples were collected. Background samples were always built with 25–30 increments of soil samples.

#### **Soil sampling strategy**

In past years the usual strategy for soil sampling consisted of sampling at firing positions, around a representative number of targets, and around suspected hot spots (broken casings, UXOs or debris, etc.). The whole characterization of training areas in Gagetown was published in 2003 and 2004 (Ref. 15, 16, 26, 48).

In this study, only the firing positions were sampled. Multi-increment samples were taken in each single sub-area illustrated in Figure 4-2 (for example, seven multi-increment samples would be taken in the entire area presented in Figure 4-2). For Site 5, a square was added from 15 to 20 m. The area closest to the gun was divided into smaller sections because we thought more residue would be deposited in that area. Surface soils were collected to a depth of 5 cm.



**Figure 4-2. Soil sampling areas relative to the gun position.**

Each soil sample was built with 25–30 increments. However, in some cases, we also collected multi-increments samples having 50 and 100 increments each. The 25- to 30-increment sampling is usually done in a small surface (e.g., in a sub-square in Figure 4-2), while the 50- or 100-increment sampling is done in large areas, for example, the area covering the section from 15 m and beyond of the gun position at Figure 4-2. In the following text, the soil samples will always refer to the 25- to 30-increment samples, while a mention will be made in the text when the number of increments was higher (50 or 100). One duplicate sample was collected for each site. All soil samples were stored in polyethylene bags.

#### **Analytical methods for soils**

For energetic materials analyses, soil samples were air-dried in the dark and then homogenized by adding acetone until the soil was completely submerged to form a slurry. The acetone was then evaporated. Soils were sieved through 25-mesh sieves ( $<710\ \mu$ ) and extracted at DRDC Valcartier according to the following procedure. Eight grams of soil were put in an amber vial and mixed with acetonitrile (10 mL). Vortex was applied for one minute, followed by a sonication period of 18 h in an ultrasonic bath in the dark. The samples were left to settle for 30 min. Acetonitrile (2 mL) was removed from the vial and diluted with water (2 mL) containing calcium chloride (1%). The mixture was filtered on a  $0.45\text{-}\mu$  filter to get 1 mL of solution ready to inject into the high-pressure liquid chromatograph (HPLC). Soil extracts were maintained at 4°C until analyzed by

HPLC according to method EPA 8330 (1994) (Ref. 42). The 14 compounds analyzed for energetic materials were HMX, RDX, 1,3,5-TNB, 1,3-DNB, NB, TNT, tetryl, NG, 2,4-DNT, 2,6-DNT, 2-Am-DNT, 4-Am-DNT, 2-NT, 3-NT, and 4-NT.

The HPLC method was preferred to the gas chromatography (GC) method since reproducible results with the GC/ECD method were difficult to achieve and concentrations expected were in the range of the mg/kg, easily achievable by the more rugged HPLC method (Ref. 11, 12). In our study, the HPLC method reached a detection limit of 0.25 mg/kg for all analytes. Detection limits were reduced to 0.06 mg/kg when the extracts were concentrated (Turbovap evaporator, Zymark Corporation, Hopkinton, Massachusetts, USA). In order to obtain lower limits of detection, 2 mL of acetonitrile from the soil extract were evaporated to dryness with a Zymark evaporator in a test tube. Thereafter, 0.5 mL of water and 0.5 mL of acetonitrile were added; this mixture was used directly for the analysis. Analyses were performed with a HPLC Agilent HP 1100 equipped with a degasser G1322A, a quaternary pump model G1311A, an autosampler G1313A, and an UV diode array detector model G1315A monitoring at 210, 220, and 254 nm. The injection volume was 20  $\mu$ L and the column used was a Supelcosil LC-8 column 25 cm  $\times$  3 mm  $\times$  5  $\mu$ m eluted with 15:85 isopropanol: water (v:v) at a flow rate of 0.75 mL/min. The column temperature was maintained at 25°C during the analysis. Standards and solvents were diluted 1:2, acetonitrile to water (0.5 mL CAN:0.5 mL water).

#### *Sampling of Residues on Plates*

Plates placed downrange of the gun barrel were set out to collect the solid particles that were thrown from the muzzle of the gun. The dimensions of the plates were 1 m  $\times$  1 m and they were slightly concave, i.e., having a small hollow in the middle of the plate to catch water or solvent during sample recovery and cleaning. The plates were never used before this trial.

#### **Sampling strategy**

The number of plates placed in front of the gun was determined by the topography of the site. Sometimes, no more than 10 plates could be accommodated and other times as many as 27 plates were used. In each case, plates were placed to cover a maximum area in front of the gun. After firing, plates were cleaned with cotton wipes wetted with acetone to recover all the residues. The wipes were placed in amber glass jars. Each jar was dedicated to one plate.

### **Analytical methods for wipes**

All bottles containing the cotton wipes were brought from the field to the laboratory without chemical or physical modification. Approximately 100 to 150 mL of acetonitrile was added to each bottle to cover the wipes. Bottles were placed on a shaker table for 18 hours and in a sonic bath for 1 hour. According to EPA method 8330 (Ref. 42), 7 mL of the extract was mixed with 7 mL of water for HPLC analysis. In some cases, the sample extracts were concentrated in a Zymark apparatus to reach lower detection limits.

### **Trials and Sampling Description**

The military training exercises were performed between 9 and 12 May 2005, at CFB Gagetown. A brief schedule of the exercise is given in Table 4-1. During the whole study, five sites were visited and sampled. The size of the area, the topography, and the availability to sample the area in front of the gun were the criteria used to select the studied gun.

**Table 4-1. Schedule of the artillery exercises sites sampled at CFB Gagetown.**

	<b>Site 2</b>	<b>Site 3</b>	<b>Site 4</b>	<b>Site 5</b>	<b>Site 6</b>
Day	Monday 9 May	Monday 9 May	Tuesday 10 May	Tuesday 10 May	Wednesday to Thursday 11–12 May
Hour	10:00 a.m. to 4:00 p.m.	10:00 a.m. to 4:00 p.m.	6:00 a.m. to 3:30 p.m.	6:00 a.m. to 3:30 p.m.	10:00 p.m. to 11:00 a.m.
Howitzer fired	LG1	C3	LG1	C3	LG1 and C3
Rounds fired	7 rounds at charge 4  7 rounds at charge 5	22 rounds at charge 4	13 rounds at charge 4	74 rounds at charge 5	34 rounds at charge 7  28 rounds at charge 7

The different kinds of 105-mm rounds fired were high explosives (HE), HE proximity, HE time, illuminating, and HE plug C32. The difference between the HE rounds is the detection method to induce the explosion at a fixed height. M1 single-base gun propellant, used in all tests, is composed of 85% NC, 10% 2,4-DNT (including 2,6-DNT as an impurity), and 5% dibutylphthalate. Other ingredients present at less than 1% are diphenylamine and potassium sulphate (Ref. 33).

The total mass of propellant burned during the exercise was determined from the number of propellant bags used to propel the munitions. Table 4-1 gives the

number of rounds with their charge and Table 4-2 gives the mass of propellant in each bag. When the number of bags used for the firing, usually named the charge, is known, the complete mass of propellant used can be calculated. For example, a firing at charge 4 means that bags 1, 2, 3, and 4 were fired into the gun chamber, totaling a mass of 467 g of propellant. Moreover, bags 1 and 2 contain single-perforation grains, while bags 3 to 7 contain seven-perforation grains. The main difference between the single- and the seven-perforation is the surface area and, consequently, the rate of burning; the single-perforation grain burns with a lower rate than a multiple-perforation grain.

**Table 4-2. Mass of propellant in bags 1 to 7 in 105-mm rounds.**

<b>Bag</b>	<b>Mass of propellant (g)</b>
1	245
2	40
3	72
4	110
5 <sup>1</sup>	114
6	260
7	406

Note 1: Bag 5 contained a piece of lead foil 114 mm × 198 mm × 0.05 mm used as a decoppering agent (Ref. 44).

### *Area Airstrip 3*

The first region visited by the military troops was Area Airstrip 3 located in Range 6 (green zone). Witness plates were placed at Sites 2, 3, and 4. The first trial was performed with 50 witness plates placed in front of an LG1 Mark II 105-mm howitzer and a C3 105-mm howitzer located in Sites 2 and 3, respectively (Fig. 4-3). These two guns were sampled at the same time (see Table 4-1). After this exercise, one part of the artillery moved to Site 4, which was at higher elevation than the other two sites (Fig. 4-4).



a. Site 2.



b. Site 3.

**Figure 4-3. Sites 2 and 3 located in Area Airstrip 3 in CFB Gagetown.**



**Figure 4-4. Site 4 located in Area Airstrip 3 in CFB Gagetown.**

#### **LG1 Mark II 105-mm howitzer at Site 2, Area Airstrip 3**

Figure 4-7 shows the locations of the 25 witness plates placed in front of the gun muzzle. Two plates were placed on each side of the muzzle at a distance of 5 m. A total of 27 plates was used. The 14 rounds fired with this gun were HE (five rounds), HE Proximity (seven rounds) and smoke (two rounds). Seven rounds were fired at charge 4 and the seven other rounds at charge 5. The ground was soft, and consequently, soil sampling was conducted in this area. The four soil backgrounds were collected on Sunday, a day before the exercise started. Since the locations of guns were unknown at that moment, the sampling was done on the complete surface area and not directly in front of the studied gun, as was the case for the other sites. Twelve samples including one duplicate were collected in front of the gun and two samples of 50 increments each were taken around the muzzle of the gun.

**C3 105-mm howitzer at Site 3, Area Airstrip 3**

Figure 4-8 describes the location of the 23 witness plates placed in front of the gun, with a distance between the plates of 5 m, covering an area of approximately  $25 \times 30$  m. The gun fired 22 rounds at charge 4, but the type of munitions fired was unknown. The composition of the ground was very similar to Site 2, i.e., sandy, making soil sampling easy. Eleven composite samples, including one duplicate, were collected in front of the gun and four soil samples of 100 increments each were taken in the complete firing zone.

**LG1 Mark II 105-mm howitzer at Site 4, Area Airstrip 3**

The topography of that site was very different from the other three. In fact, the surface in front of the guns was covered by 2-ft-tall grass with some surface water that made the positioning of the witness plates and the sampling difficult. For this reason, no soil sampling was done at this site. Twenty-three aluminum plates were placed in front of the LG1 Mark II 105-mm howitzer (Fig. 4-4 and 4-9). Finally, 13 rounds of 105-mm at charge 4 were fired.

*C3 105-mm Howitzer at Site 5*

Site 5 (Fig. 4-5) was located in the Red Impact Area in the Dingee Wood Range, approximately 1 km south of the Area Airstrip 3. Twenty-seven aluminum plates were placed in front of the C3 105-mm howitzer as described in Figure 4-10. Seventy-four rounds of 105-mm at charge 5 were fired. Soil sampling was also conducted at Site 5. Twelve composite samples, including one duplicate, were collected in front of the gun, while two soil samples of 50 increments each were taken around the gun position.

*Hersey Impact Area*

For the last two days, the entire artillery troop was moved to the north entrance of the Hersey Impact Area, Site 6 in this study (Fig. 4-6). Two guns, one LG1 Mark II 105-mm howitzer and one C3 105-mm howitzer, were chosen for our study and the details of each sampled site are described in the following paragraphs. The topography of the site was different from other sites because at approximately 15 m in front of the gun, beyond a sand butte, a steep vertical drop was followed by a plain, the Hersey impact area. Soil samples were collected both before and after the guns were fired.



**Figure 4-5. Site 5 located in the Dingee Wood Range in CFB Gagetown.**

#### **LG1 Mark II 105-mm howitzer at Site 6**

Ten witness plates were placed in front of the muzzle of the gun. Figure 4-11a describes the pattern adopted to place them in front of the gun. Twenty-eight rounds were fired at charge 7 and the detail of the munitions is the following: 11 HE, 12 HE proximity, two HE time, and three illuminating. One background sample (the delay before they started firings had limited the number of backgrounds) and four multi-increment samples were taken in the firing position before and after the exercise, respectively.

#### **C3 105-mm howitzer at Site 6**

Eight aluminum plates were placed in front of the muzzle of the gun. Figure 4-11b describes the pattern adopted to place them in front of the gun. In that case, 34 rounds were fired at charge 7 and the detail of the munitions used is as follows: 15 HE and 19 HE plug C32. Moreover, three soil background samples and three multi-increment samples were collected in front of the gun.



a. Entire area.



b. Witness plates in front of the gun.

Figure 4-6. Site 6.

## Results

This section presents results from the sampling with witness plates and from the soil sampling. The advantage of using the plates is that the collected contamination comes from the current firing, while the soil may have been contaminated by previous firing exercises. However, the soil sample results were considered as supplementary and complementary data.

Residue data from the witness plates were used to estimate the mass of residues deposited by firing activities. The total mass of propellant burned during the exercise was determined from the number of propellant bags used to propel the munitions. The mass of residues deposited relative to the mass of propellant in each bag (see Table 4-2) was used to calculate the percentage of propellant residues deposited into the environment by the firing of these munitions. The mass is underestimated, because not all of the residue was collected by the plates and the total affected area was difficult to evaluate.

Soil sampling was performed to compare the results from soil accumulation versus plate deposition of the propellant residues produced after a live firing. Results only estimate the masses of residues since the soil residues concentrations were heterogeneous. Soil samples were collected at Sites 2, 3, 5, and 6. Soil sampling was not done at Site 4 because of the vegetation cover.

### *Sampling at Sites 2, 3, and 4 at Area Airstrip 3*

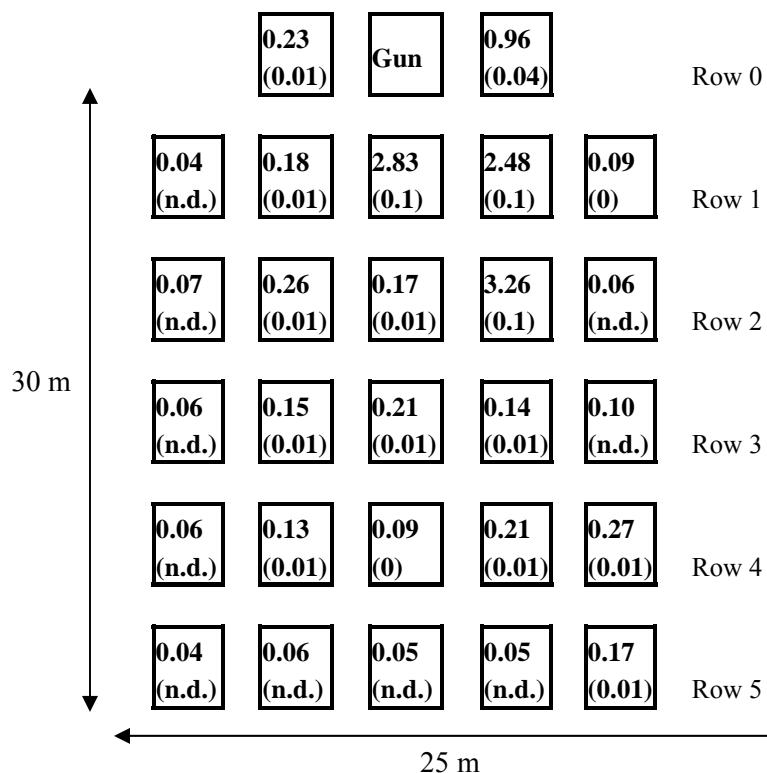
#### **LG1 Mark II 105-mm howitzer at Site 2**

Figure 4-7 shows the residues distribution at Site 2. Masses of 2,4-DNT and 2,6-DNT (in parentheses) are presented. Significant quantities of 2,4-DNT on each side of the gun were measured and the contamination was concentrated in front of the gun. The concentration of residues was higher on the left side of the gun when looking in the firing direction from the gun position, probably as a result of wind direction. Finally, the results obtained for the plates located at the extremities of the sampling area indicated that the area covered by the plates was not large enough to catch the entire plume since detectable levels of DNT were still present on the plates farthest from the gun.

Fourteen rounds at charges 4 and 5 (seven rounds each) were fired, representing 467 and 581 g of propellant, respectively, for each shot. To obtain this value, for a charge 4, for example, one sums the mass in bags 1 through 4 (Table 4-2). We calculated that 7336 g of propellant was burned during this exercise. Since 10% of the propellant is 2,4-DNT, up to 733.6 g of 2,4-DNT were present in the gun propellant. 2,6-DNT is an impurity in the production of 2,4-DNT and represents 5% of the total mass of DNT collected. Ninety-one percent of the

DNT was found in the first three rows. The total quantity of DNT, including the 2,6-DNT, was used for the calculation. A mass of 12.94 mg was collected on the 27 aluminum plates that covered a surface of approximately 25 by 30 m, i.e., 750 m<sup>2</sup>. The mass collected for 27 m<sup>2</sup> (27 plates of 1 m<sup>2</sup> each) was 12.94 mg; therefore 360 mg of residues was dispersed over the total area. It was assumed that the distribution of residues is the same over the unsampled area. This result means that 0.05% of the total mass of fired DNT was deposited on the soil in front of the gun.

Ten of the 27 plates showed very low concentrations of RDX (maximum of 0.1 mg/m<sup>2</sup> and minimum of 0.0005 mg/m<sup>2</sup>). These results are not included in Figure 4-7 because the contamination did not come from the current activity but probably from soil particles contaminated by past firing activities projected on the plates by the wind or the blast created by the gun.



**Figure 4-7. Masses (mg) of 2,4-DNT and 2,6-DNT (in parentheses) collected on the witness plates at Site 2 (n.d.= not detected).**

**Table 4-3. Concentrations of RDX, TNT, 2,4-DNT, and 2,6-DNT in soil samples collected at Site 2.**

Sample	RDX (mg/kg)	TNT (mg/kg)	2,4-DNT (mg/kg)	2,6-DNT (mg/kg)
Background				
Site 2, sample 1	—	—	11.8	—
Site 2, sample 2	—	—	1.3	—
Site 2, sample 3	1.44	1.0	0.4	—
Site 2, sample 4	—	—	0.5	—
Mean value*	—	—	3.5	
After firing				
Site 2, GP-1	—	—	47.3	2.1
Site 2, GP-2	—	—	55.1	2.7
Site 2, 0-5 m -A	—	—	53.3	3.2
Site 2, 0-5 m A DUP	—	—	34.5	1.4
Site 2,0-5 m B	—	—	49.0	2.4
Site 2, 0-5 m C	—	—	19.7	—
Mean value	—	—	43.15	2.33
Site 2, 5-10 m A	—	—	21.2	—
Site 2, 5-10 m B	2.6	—	28.8	—
Site 2, 5-10 m C	—	—	10.3	—
Mean value*	—	—	20.1	—
Site 2, 10-15 m	—	—	6.3	—
Site 2, 15-20 m	4.3	2.8	4.4	—
Site 2, 20-X m-1	—	—	2.6	—
Site 2, 20-X m-2	0.4	—	23.2	—
Site 2, 20-X m-3	—	—	6.3	—
Mean value*	—	—	10.7	—

\* Mean value is not calculated when only one datum is available.

Table 4-3 shows the soil concentrations at Site 2. A day before the trial, four background composite samples (Site 2 samples 1, 2, 3, and 4) were taken in the whole area and a mean concentration of 2,4-DNT of 3.5 mg/kg was obtained. This result was significantly lower than the quantities of 2,4-DNT found between 0 and 5 m from the muzzle of the gun, with an average concentration of 43 mg/kg. The two samples collected at the gun position (2-1-GP) were grouped with the region between 0 and 5 m. Region C, located on the left site of the gun, contained less contamination than regions A and B; this is in accordance with the trend observed with the aluminum plates (see Figure 4-2). The mean concentration of 2,4-DNT observed between 5 and 10 m was 20 mg/kg, which is 50% less

than the contamination found in the first region (0–5 m). The two other sections, between 10 and 15 m and 15 and 20 m, showed lower concentrations of 2,4-DNT, with 6 and 4 mg/kg, respectively. Finally, the three composites of 50 increments, named 2-1-20-X m-1, 2, and 3 collected at 20 m and farther from the gun (X means that the end distance is unknown), showed significant concentrations of 2,4-DNT with an average value of 10.7 mg/kg.

2,6-DNT was detected for the five highest concentrations of 2,4-DNT only. The percentages of 2,6-DNT relative to the total mass of DNT were between 4 and 5.6%, similar to the percentages observed in residues collected on the witness plates.

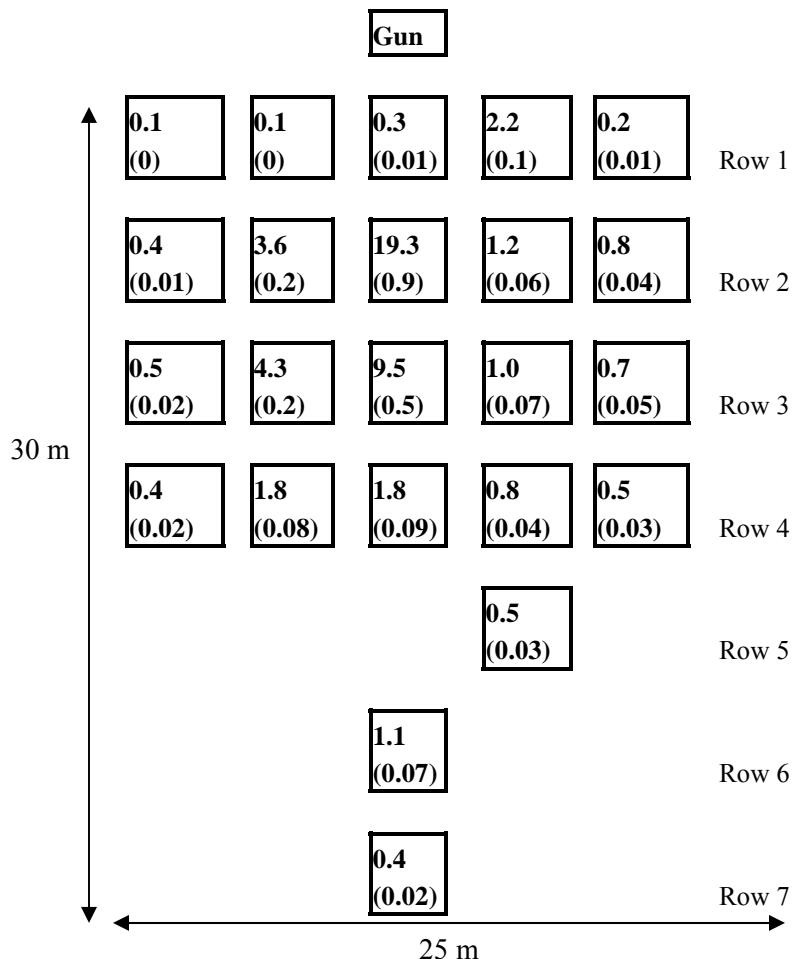
### C3 105-mm howitzer at Site 3

Figure 4-8 shows slightly higher contamination on the right side of the gun when looking in the firing direction from the gun position, but most of the 2,4-DNT was dispersed directly in front of the gun muzzle. As for Site 2, the results obtained for the plates located at the extremities of the rows indicated that the area covered by the plates was not large enough because detectable levels of 2,4-DNT were found on those plates.

Twenty-two rounds at charge 4 were fired, representing 10,274 g of propellant, of which 10% was 2,4-DNT (1027.4 g). Masses of 51.5 mg and 2.56 mg of 2,4- and 2,6-DNT, respectively, were collected on the whole surface, i.e., on the 23 aluminum plates covering an area of approximately 25 by 30 m ( $750\text{ m}^2$ ). The 2,6-DNT represents 4.7% of the total mass of 2,4- and 2,6-DNT collected. Eighty-six percent of 2,4-DNT was observed in the first three rows. As previously, the total mass of DNT was used in the calculation. Since 54.06 mg of DNT was found on a  $23\text{-m}^2$  area, by extrapolation 1762.8 mg of DNT should occur for the whole surface of  $750\text{ m}^2$ . This result means that 0.2% of the initial DNT charge was deposited into the environment in front of the gun. At Site 3, only one plate showed soil contamination by RDX with a concentration of  $0.002\text{ mg/m}^2$ .

Results obtained for the soil sampling done in front of the C3 105-mm howitzer at Site 3 are listed in Table 4-4. A concentration of 2,4-DNT of 1.06 mg/kg was obtained for the background sample taken before the firings (Site 3-BG-1), while a mean concentration of 2,4-DNT of 16.92 mg/kg was detected between 0 and 5 m from the muzzle of the gun. The mean contamination of the first two regions, 0–5 m and 5–10 m, was not significantly different. In fact, 16.92 and 21.02 mg/kg were found for these two regions, respectively. The mean value calculated for the area from 10 m and farther dropped to 2 mg/kg. The results obtained for the sample «Site 3, 10–15 m» and its duplicate were significantly different, an indication that the soil contamination was not homogene-

ously distributed. Therefore, underestimation or overestimation of the contamination was easily possible.



**Figure 4-8. Masses (mg) of 2,4-DNT and 2,6-DNT (in parentheses) collected on the witness plates at Site 3.**

**Table 4-4. Concentration of 2,4- and 2,6-DNT in soil samples collected at Site 3.**

Sample	2,4-DNT mg/kg	2,6-DNT mg/kg
Site 3-BG-1	1.06	—
Site 3, 0–5 m A	10.75	—
Site 3, 0–5 m B	15.86	0.38
Site 3, 0–5 m C	24.14	0.65
Mean value	16.92	0.52
Site 3, 5–10 m A	61.82	1.05
Site 3, 5–10 m B	0.77	—
Site 3, 5–10 m C	0.49	—
Mean value	21.02	1.05
Site 3, 10–15 m	1.90	—
Site 3, 10–15 m DUP	5.23	—
Site 3, 15-X m-1	1.35	—
Site 3, 15-X m-2	0.73	—
Site 3, 15-X m-3	0.99	—
Mean value	1.02	—
Site 3-A	40.02	0.97
Site 3-B	37.39	1.16
Site 3-C	58.05	1.99
Site 3-D	29.26	0.81
Mean value	41.18	1.23

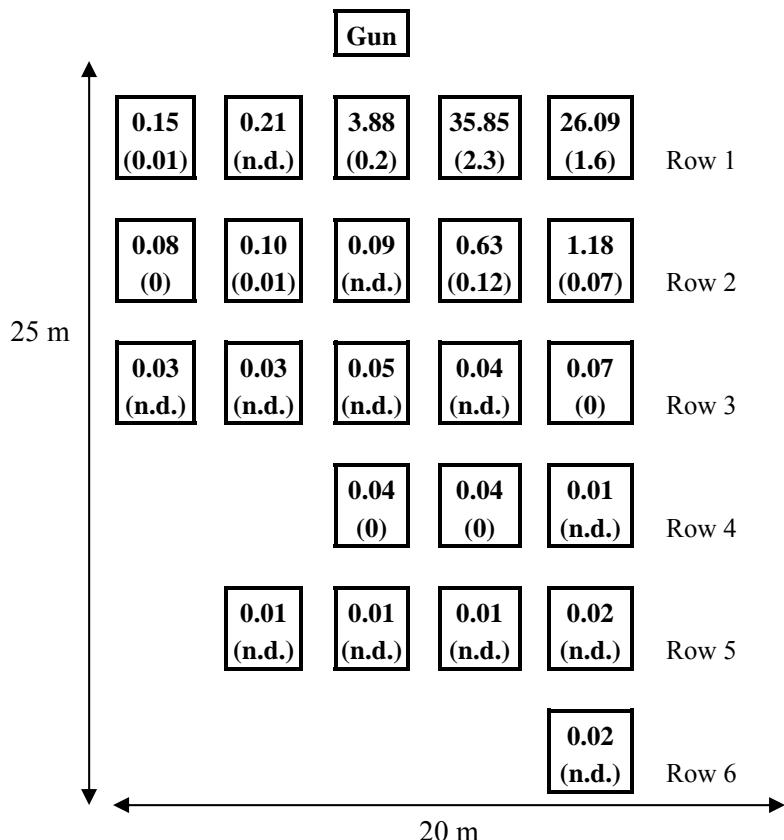
The four samples of 100 increments named Sites 3-A, B, C, and D collected in the complete surface (40 m by 100 m) behind and in front of the gun showed very high concentrations of 2,4-DNT, which means that, after the exercise, this compound is present everywhere on the surface. In fact, the mean value obtained for the whole region was 41.18 mg/kg, higher than concentrations found directly in front of the gun.

In samples containing a concentration higher than 15 mg/kg of 2,4-DNT, 2,6-DNT was detected. The percentages of 2,6-DNT relative to the total mass of DNT were between 2 and 3%. Finally, no RDX, TNT, HMX, nor 1,3,5-TNB was detected in soil samples.

#### **LG1 Mark II 105-mm howitzer at Site 4**

Figure 4-9 describes the distribution of 2,4-DNT and 2,6-DNT in front of the gun at Site 4 after the use of 6071 g of gun propellant for firings. The contamina-

tion was significantly higher on the left side of the gun when looking in the firing direction from the gun position and the wind direction is an explanation for this observation. No significant concentration of 2,4-DNT was found in the plates of rows 3, 4, 5, and 6. Thirteen rounds of 105-mm at charge 4 were fired utilizing 6071g of propellant, including 607.1 g of 2,4-DNT. The mass of 2,6-DNT represents 5.9% of the total mass of DNT. However, 99% of the 2,4-DNT was found between rows 1 to 3. In the 23 plates ( $23 \text{ m}^2$ ), 72.97 mg of DNT was collected and, consequently, by extrapolation, 1586.3 mg of DNT was found on the total area of  $500 \text{ m}^2$  ( $25 \times 20 \text{ m}$ ). This result means that 0.3% of DNT was expelled in front of the gun.



**Figure 4-9. Masses (mg) of 2,4-DNT and 2,6-DNT (in parentheses) collected on the witness plates at Site 4 (n.d.= not detected).**

Soil contamination was observed. In fact, HMX and 1,3,5-TNB were found once with a value  $0.0003$  and  $0.002 \text{ mg/m}^2$ , respectively, while RDX and 1,3-DNB were detected in three and five samples, respectively, with concentrations as low as those for HMX and 1,3,5-TNB. TNT was also present in 11 samples

with a maximum value of 0.017 mg/m<sup>2</sup>. This contamination results from past military activities and is most probably affecting our analysis through particles being projected onto the plates by the wind or the muzzle blast.

Gun				
0.3 (0.04)	0.2 (0.01)	3.2 (0.1)	21.7 (1.4)	31.1 (2.1)
0.2 (0.01)	0.1 (0)	0.7 (0.02)	8.4 (0.4)	13.8 (0.7)
0.1 (0)	0.2 (0.01)	0.3 (0.01)	2.7 (0.1)	2.6 (0.1)
0.1 (0)	0.1 (n.d.)	0.2 (0.01)	0.2 (0.01)	1.4 (0.07)
0.05 (n.d.)	0.1 (n.d.)	0.1 (0)	0.1 (0.01)	0.2 (0.01)
Row 1				
Row 2				
Row 3				
Row 4				
Row 5				
Row 6				
Row 7				

**Figure 4-10. Masses (mg) of 2,4-DNT and 2,6-DNT (in parentheses) collected on the witness plates at Site 5 (n.d.= not detected).**

### C3 105-mm Howitzer at Site 5

The concentrations of 2,4-DNT and 2,6-DNT found in front of the gun can be observed in Figure 4-10. The distribution shows that contamination was significantly higher on the left side of the gun when looking in the firing direction from the gun position, as was the case for Site 4. Ninety-seven percent of 2,4-DNT was found in Rows 1, 2, and 3. Consequently, low concentrations of 2,4-

DNT were found in the plates of Rows 4, 5, 6, and 7. That shows that the plates were located far enough from the gun to establish most of the contamination plume. However, the results obtained for the plates located on the left side of the zone definitively show that it would be necessary to place more plates in this region. Significant quantities of 2,4-DNT would probably be found on plates on the left side, i.e., the contamination exceeded the studied area.

The most intense firing was conducted at Site 5. Seventy-four rounds at charge 5 were fired for a total mass of propellant of 42.994 kg, including 4299.4 g of DNT. The total mass of 2,6-DNT represents 5.5% of the collected DNT. A mass of 93.49 mg of DNT was measured on a surface area of 27 m<sup>2</sup>, corresponding to the 27 plates. For the entire surface area of 625 m<sup>2</sup>, 2164.12 mg was obtained by extrapolation. This result means that 0.05% of the total mass of DNT was dispersed into the environment in front of the gun. Since site access during the exercise was not permitted, sampling took place only at the completion of the exercise. Considering the long time period between the first fired rounds and the sampling, it may be assumed that many particles were lost by displacement due to wind or blast from firings.

Soil contamination was also found on eight plates at Site 5. Two plates showed concentrations of 1,3,5-TNB with a maximum concentration of 0.03 mg/m<sup>2</sup>, RDX was present in five plates with a maximum of 0.002 mg/m<sup>2</sup>, and TNT was found in four plates with a maximum of 0.63 mg/m<sup>2</sup>.

Results obtained for soil samples collected at Site 5 are listed in Table 4-5. The contamination by 2,4-DNT observed at this site was lower than for Sites 2 and 3. Even for samples between 0 and 5 m from the muzzle of the gun, only one soil sample showed 2,4-DNT with a concentration of 1.01 mg/kg compared to 10 mg/kg and higher for Site 3. Even if the contamination was low, the highest concentrations of 2,4-DNT were still detected in the area between 0 and 10 m from the muzzle and around the gun position.

No 2,6-DNT, RDX, TNT, or 1,3,5-TNB were detected. These results are not in agreement with the contamination found in the aluminum plates because eight plates showed concentrations of 1,3,5-TNB, RDX, and TNT. For 2,6-DNT, the result is in accordance with the previous sections that showed that 2,6-DNT was detected only when concentration of 2,4-DNT was sufficiently high, i.e., higher than 15 mg/kg.

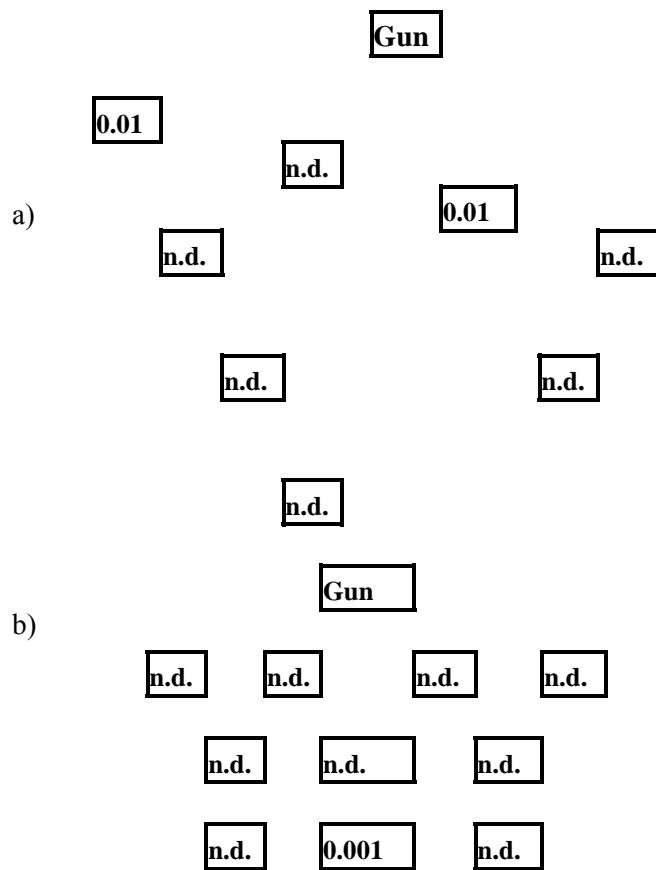
**Table 4-5. Concentration of 2,4-DNT soil samples collected at Site 5.**

<b>Sample</b>	<b>2,4-DNT (mg/kg)</b>
Site 5, GP-1	0.40
Site 5-GP-2	0.62
Site 5, 0–5 m A	1.01
Site 5, 0–5 m B	—
Site 5, 0–5 m C	—
Site 5, 5–10 m A	1.07
Site 5, 5–10 m B	0.31
Site 5, 5–10 m B DUP	—
Site 5, 5–10 m C	—
Site 5, 10–15 m	—
Site 5, 15–20 m	—
Site 5, 20-X-1	—
Site 5, 20-X-2	—
Site 5, 20-X-3	—

***LG1 Mark II 105-mm Howitzer and C3 105-mm Howitzer at Site 6***

The two guns were selected from among the whole battery for their accessibility and feasibility to sample in front of the gun. During this last exercise, the weather was rainy and windy, causing a direct effect on the results. Even though the LG1 Mark II and the C3 fired 28 rounds at charge 7 (34.92 kg of propellant) and 34 rounds at charge 7 (42.40 kg of propellant), respectively, no contamination was detected on the plates (Fig. 4-11). The probability that the pattern adopted to place the plates was responsible for this result is low because the plates were close enough to the gun, covering a significant surface area, and they should have caught some contamination, as with previous patterns.

Soil contamination was found on four plates located in front of the LG1 Mark II 105-mm howitzer. A low concentration of HMX (0.001 mg/m<sup>2</sup>) was detected on plate 5; plate 8 contained traces of TNT, RDX, and 1,3,5-TNB with concentrations of 0.173, 0.0003, and 0.001 mg/m<sup>2</sup>, respectively, while HMX and TNT were found on plate number 9 with concentrations of 0.004 and 0.011 mg/m<sup>2</sup>, respectively. Finally, traces of RDX, i.e., 0.0005 mg/m<sup>2</sup>, were detected on one plate.



a. LG1 Mark II 105-mm howitzer.

b. C3 105-mm howitzer.

**Figure 4-11. Mass (mg) of 2,4-DNT collected on the witness plates at Site 6 (n.d.= not detected). Note: No 2,6-DNT was detected at Site 6.**

The results from soil sampling done in front of the LG1 Mark II and C3 105-mm howitzer are grouped in Table 4-6. In both cases, the area in front of the gun was too short to apply the pattern described in Figure 4-2. Therefore, soil samples were built with 50 increments each taken in the complete area in front of the gun. Results obtained for the backgrounds (BG) and the samples are similar. Consequently, the 2,4-DNT detected cannot be confirmed to originate from the current exercise. No 2,6-DNT, HMX, TNT, RDX, or 1,3,5-TNB were detected in these soil samples. These results are not in agreement with the contamination found in the aluminum plates since these compounds were found in four plates located in front of the LG1 Mark II 105-mm howitzer.

**Table 4-6. Concentration of 2,4-DNT in soil samples collected at Site 6.**

Sample	2,4-DNT (mg/kg)
<b>C3 105-mm howitzer</b>	
Site 6-C3-BG 1	1.77
Site 6-C3-BG 2	0.44
Site 6-C3-BG 3	0.12
Site 6-C3-1	0.52
Site 6-C3-2	0.48
Site 6-C3-3	0.90
<b>LG1 Mark II 105-mm howitzer</b>	
Site 6-LG1-BG	1.07
Site 6-LG1-1	0.15
Site 6-LG1-2	0.23
Site 6-LG1-3	0.08

*Summary*

Table 4-7 presents the details and results obtained from witness plates sampling at each site. Only M1 single-base propellant was used for the firings. Consequently, the main residue dispersed in front of the gun was 2,4-DNT. Table 4-7 clearly shows that the type of gun and the number of rounds did not influence the percentage of residue. However, the charge used, i.e., the quantity of propellant used for each firing, influenced the residue concentration. In fact, the larger the mass of gun propellant used for a firing, the lower the percentage of residue dispersed in front of the gun.

**Table 4-7. Results obtained at each site from sampling with witness plates.**

Type of 105-mm howitzer	Number of rounds	Charge	Propellant load (g)	Mass of DNT (g)	Residue (mg)	Surface area (m <sup>2</sup> )	% residue
LG1 (Site 2)	14	4 and 5	7336	733.6	52.4	750	0.05%
LG1 (Site 4)	13	4	6071	607.1	1586.3	500	0.3%
LG1 (Site 6)	28	7	34920	3492	0.02	—	0%
C3 (Site 3)	22	4	10274	1027.4	1762.8	750	0.2%
C3 (Site 5)	74	5	42994	4299.4	2164.12	625	0.05%
C3 (Site 6)	34	7	42400	4240	0.001	—	0%

**Table 4-8. Concentration of 2,4- and 2,6-DNT in soil samples collected at Sites 2, 3, and 5.**

Sample	2,4-DNT mg/kg	2,6-DNT mg/kg
Site 2-BG-1	3.5	—
Site 2, 0–5 m	43.15	2.33
Site 2, 5–10 m	20.1	—
Site 2, 10–15 m	6.3	—
Site 2, 15–20 m	4.4	—
Site 2, 20-X m	10.7	—
Site 3-BG-1	1.06	—
Site 3, 0–5 m	16.92	0.52
Site 3, 5–10 m	21.02	—
Site 3, 10–15 m	1.90	—
Site 3, 10–15 m DUP	5.23	—
Site 3, 15-X m	1.02	—
Site 5, 0–5 m	0.4	—
Site 5, 5–10 m A	0.5	—

Table 4-8 presents the results obtained from soil sampling at Sites 2, 3, 5, and 6. For Site 5, data for only the first two layers (0–5 m and 5–10 m) are given because residues were not detected in the other surface areas. No residues were detected at Site 6, since background values were similar to the concentrations in soil samples. Table 4-8 mainly shows two trends: 1) At Sites 2 and 3, the 2,4-DNT was concentrated in the first 10 m from the gun position; 2) Residues concentrations were lower at Sites 5 and 6 than at Sites 2 and 3. These two observations also were reported from the study with the witness plates.

## Discussion

The trial performed at CFB Gagetown allowed the study of the dispersion of residues around and in front of guns after numerous firings. Residues from firing positions for three LG1 Mark II 105-mm howitzers and three C3 105-mm howitzers were sampled using witness plates at Sites 2, 3, 4, 5, and 6. The two major contaminants were 2,4-DNT and 2,6-DNT. The 2,6-DNT, an impurity in the production of 2,4-DNT, was often detected on the witness plates and represented approximately 5% of the total DNT.

The highest quantities of DNT were found in the first three rows in front of and on each side of the gun. Therefore, most of the contamination is located just beside the gunners.

At Site 5, low concentrations of 2,4-DNT were observed; this was unexpected since the greatest amounts of propellant were fired there. However, at Site 5, even if the concentrations of 2,4-DNT were lower than expected, the contamination was concentrated in the first rows, as observed for Sites 2, 3, and 4. At Site 6, no contamination was detected on most of the plates. The weather at the end of the week was windy and rainy, and this may explain these results. Soil contaminations by RDX, HMX, TNT, and 1,3,5-TNB were observed on most of the plates.

In Table 4-9, the percentages of DNT deposited in front of the gun were grouped by site. The number of rounds fired with the charge is also given. From these results, the type of gun did not seem to affect the quantity of residues. In fact, the percentages of residues obtained from these guns were similar. Moreover, the number of rounds did not seem to influence the percentage of DNT found on the witness plates. In fact, at Site 5, the highest number of rounds was fired and the percentage of residues was low. However, the charge used for the firings seems to have an effect on the percentages recovered. In fact, the highest percentages were found at Sites 3 and 4, where the charge was the lowest (four bags). The comparison of Site 2 with the results at other sites is difficult since both charges 4 and 5 were used. Finally, at Site 6, no contamination was detected. Site 6 was the only site where the maximum charge, i.e., seven bags, was used for all firings.

In a preliminary study performed in 2003 at RDDC Valcartier by Dubé et al. (Ref. 30), the percentage of propellant recovered was in the same order of magnitude as those reported in this report. After 10 rounds at charge 4 with an LG1 Mark II 105-mm howitzer, they found 0.56% of the total fired 2,4-DNT in front of the muzzle in an area of 42 m<sup>2</sup>.

**Table 4-9. Calculated percentages of recovered DNT dispersed in front of the gun in each site.**

Site	# Rounds with the charge	C3 105-mm howitzer	LG1 Mark II 105-mm howitzer
Site 2	7 rounds at charge 4 7 rounds at charge 5		0.05%
Site 3	22 rounds at charge 4	0.2%	
Site 4	13 rounds at charge 4		0.3%
Site 5	74 rounds at charge 5	0.05%	
Site 6	34 rounds at charge 7	0%	
Site 6	28 rounds at charge 7		0%

Walsh et al. (Ref. 31) studied the residues from live-fire detonations of 155-mm howitzer rounds on snow in 2005. From three 100-increment snow samples, they estimated that 110, 19, and 86 mg of 2,4-DNT were dispersed by the firing of 60 rounds over a surface area of 30 by 30 m ( $900\text{ m}^2$ ). For each firing, 2.8 kg of single-base propellant was consumed, thus indicating that full charge was always used. For Site 5, we estimated a dispersion of 3116 mg of DNT for an area of  $900\text{ m}^2$  after 74 rounds at charge 5, corresponding to 581 g of single-base propellant for each firing. Our results demonstrate that the contamination was significantly more important in our study. However, many factors could explain this difference: the weather (wind and rain), the type of soil, the vegetation, the charge used for the firing, and the type of propellant. Furthermore, different guns were used and the quantity of propellant used per firing was higher with the 155-mm (2.8 kg) than for the 105-mm, even at full charge (1.25 kg). Walsh et al. (Ref. 31) also found that the 2,4-DNT was more concentrated in the region between 0 and 10 m from the gun.

In the second part of the study, soils were characterized at Sites 2, 3, 5, and 6. At Sites 2 and 3, significant concentrations of 2,4-DNT were found and the concentrations were highest close to the gun. The highest concentration was detected at Site 3 between 5 and 10 m from the muzzle of the gun (61.82 mg/kg). At Sites 2 and 3, the effect of the firings on soil contamination was significant because 3.5 and 1 mg/kg of 2,4-DNT were detected, respectively, before the trial, while the average concentrations of 26 and 19 mg/kg were found, respectively, in soil samples in the region after the firings of 0 to 10 m from the gun. An additional observation was that 2,6-DNT was detected only when concentrations of 2,4-DNT in soil samples were higher than 15 mg/kg.

At Site 5, the concentrations of 2,4-DNT were lower than expected, but exhibited the same trend as observed for Sites 2, 3, and 4, i.e., the contamination

was greater close to the gun. However, at Site 6, background samples and samples collected after the firings gave similar results. The weather, the morphology of the site, and the type of soil may explain this last observation. As no tree nor grass was present at these sites, the wind may have been more efficient at dispersing the contamination compared with Sites 2, 3, and 4, where little trees and long-grass covered the soil, thereby probably preventing the wind from blowing away the particles. Moreover, the type of soil was different at Sites 5 and 6, and that may affect the extraction method. In fact, the soil was sandy and the specific surface was higher than for dirt and, consequently, the interaction between organic matter and the analyzed compounds may increase with the contact surface. That may explain why low concentrations of 2,4-DNT and no 2,6-DNT, HMX, RDX, TNT, and 1,3,5-TNB were found in soil samples collected at Sites 5 and 6. Moreover, the low concentrations of DNT could be explained by the fact that at Sites 5 and 6, firings were performed at charges 5 and 7 and the residues could be less important because, at this charge, a more complete combustion existed.

Chemical compounds such as HMX, RDX, TNT, and 1,3,5-TNB were often found on the aluminum plates, but not in the soil. The interaction between the soil and the chemical compounds could probably explain that the extraction of contaminant by acetonitrile may be less efficient from soil samples than from cotton wipes that do not contain other organic matter that can interact with the analytes. It is also important to mention that just a small quantity (4 or 8 g) of the soil was taken for the extraction and, consequently, if the distribution of the contamination was not homogeneous, no compound could be detected even if contamination was present in the soil. Adding acetone to the soil to make a slurry had demonstrated its efficiency, but residues embedded in NC fibers can be difficult to dissolve and, consequently, underestimate the mass of residues measured in soil samples. In fact, with the duplicate, it was often demonstrated that results obtained from the same region could be significantly different.

In 2001 Jenkins et al. (Ref. 17) studied soil contamination that occurred in front of two 105-mm howitzers that fired 600 rounds each during six weeks. The size of the sampled areas in front of the two guns was 80 m<sup>2</sup> and 320 m<sup>2</sup>, respectively, and the contamination of 2,4-DNT was between 982 and 237 000 µg/kg (or 0.982 and 237 mg/kg). These results are in accordance with our values, even if the maximum concentration of 2,4-DNT found in their study was higher than the current data; the number of rounds fired in 2001 was significantly higher than the number fired in the current exercise.

Walsh et al. (Ref. 25) studied the residues dispersion provided by the firing of 100 105-mm rounds and they found that even at a distance of 50 m from the

gun, 2,4-DNT was still detected and that the distribution was also heterogeneous. Finally, the sampling was done in a sparsely vegetated gun position and in a vegetated gun position. The 2,4-DNT was found in the subsurface only at the sparsely vegetated gun position. The conclusion was that “the organic matter in the vegetated soil would be expected to sorb any 2,4-DNT that dissolves in the surface moisture.”

## Conclusions

The highest residue concentrations were observed at Sites 3 and 4 with percentages of 0.2 and 0.3%, respectively, of DNT relative to the total amount of DNT fired during the exercise. Many factors influenced the amount of residues collected. In fact, it was often noted with the results on plates that the wind affected the residues distribution on the surface. From the soil sampling, interesting results also were obtained for Sites 2 and 3; concentrations up to 61.8 mg/kg were obtained in the first 10 m in front of the gun. With plates, it was also observed that the contamination was concentrated directly in front of the muzzle.

For Sites 5 and 6, the measured concentrations were lower than expected. The weather conditions, the method of extraction (cotton wipes versus soil medium), and the number of charges consumed for the firings could explain this last observation. However, the number of bags of gun propellant used for firings was larger at these sites. Therefore, the combustion of the propellant may be more efficient when the mass of the propellant is larger. Consequently, the residues concentrations were lower than for firings with a lower quantity of propellant. Also, when results were compared for the two types of guns, it was not possible to determine which gun was most environmentally friendly because the results of these two types of guns were similar.

Comparison of witness plates and soil results was difficult since the distribution of residues in the soil was heterogeneous and the plates were subject to residue loss and redistribution by the wind. A future trial should be conducted in a closed vessel to allow all the particles to be caught during the firing. In future work, the sampled area should be expanded in order to reach the boundary of the plume and obtain a more reliable estimation of the dispersed DNT.

The particles expelled by the muzzle of the gun are in significant amounts near the gun. Furthermore, the products expelled may be dangerous for the health of the gunners, since they might be directly exposed to the contamination plume. No analysis was made directly for the gunner’s health. The gunner’s proximity to the highest residues concentrations found during our tests indicates that further studies of the health risks associated with this situation are warranted.

## References

1. **Thiboutot, S., G. Ampleman, P. Dubé, T.F. Jenkins, M.E. Walsh, J. Hawari, B. Spencer, and L. Paquet** (1998) Protocol for the Characterization of Explosives Contaminated Sites, DREV R-9721, UNCLASSIFIED.
2. **Thiboutot, S., G. Ampleman, and A. Hewitt** (2002) Guide for Characterization of Sites Contaminated with Energetic Materials, ERDC-CRREL TR-02-01, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
3. **US EPA** (1993) Approaches for the Remediation of Federal Facility Sites Contaminated with Explosives or Radioactive Wastes, EPA Handbook EPA/625/R-93/013.
4. **Checkai, R.T., M.A. Major, R.O. Nwanguma, C.T. Phillips, and M.C. Sadusky** (1993) Transport and Fate of Nitroaromatic and Nitramine Explosives in Soils from Open Burning/Open Detonation Operations, Edgewood Research Development & Engineering Center, ERDEC-TR-136.
5. **Jenkins, T.F., and M.E. Walsh** (1987) Development of an Analytical Method for Explosive Residues in Soil, CRREL Report 87-7, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire, USATHMA Report AMXTH-TE-FR-86102.
6. **Jenkins, T.F., C. Bartolini, and T.A. Ranney** (2003) Stability of CL-20, TNNAZ, HMX, RDX, NG, and PETN in Moist, Unsaturated Soil, ERDC/CRREL TR-03-7, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
7. **Miyares P.H., and T.F. Jenkins** (2000) Estimating the Half-Lives of Key Components of the Chemical Vapor Signature of Land Mines, ERDC/CRREL TR-0-17, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
8. **Ampleman, G., S. Thiboutot, S. Désilets, A. Gagnon, and A. Marois** (2000) Evaluation of the Soils Contamination by Explosives at CFB Chilliwack and CFAD Rocky Point, DREV Report TR-2000-103, Defence Research and Development Canada-Valcartier, Quebec, UNCLASSIFIED.

9. **Thiboutot, S., G. Ampleman, A. Gagnon, and A. Marois** (2000) Characterization of an Unexploded Ordnance Contaminated Range (Tracadie Range) for Potential Contamination by Energetic Materials, DREV Report TR-2000-102, Defence Research and Development Canada-Valcartier, Quebec, UNCLASSIFIED.
10. **Stamfli, N., M.A. Carrier, R. Martel, and R. Lefebvre** (2003) Initial Study of Terrestrial Forces Training Sites Potentially Contaminated by Energetic Materials, CFB Gagetown, Prepared for Defence Research Establishment Valcartier (DREV), INRS-ETE Report.
11. **Walsh, M.E., and T.A. Ranney** (1998) Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Water using Solid Phase Extraction and GC-ECD, CRREL Report 98-2, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
12. **Walsh, M.E., and T.A. Ranney** (1999) Determination of Nitroaromatic, Nitramine, and Nitrate Ester Explosives in Soils Using GC-ECD, CRREL Report 99-12, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
13. **Thiboutot, S., G. Ampleman, T.F. Jenkins, M.E. Walsh, P.G. Thorne, T.A. Ranney, and C.L. Grant** (1997) Assessment of Sampling Strategy for Explosives-Contaminated Soils. In Proceedings of the 90th Annual Air and Waste Management Society Meeting, Paper 94-WP 101.08, Toronto.
14. **Jenkins, T.F., M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, T.A. Ranney, and C.L. Grant** (1997) Assessment of Sampling Error Associated with Collection and Analysis of Soil Samples at a Firing Range Contaminated with HMX, CRREL Special Report 97-22, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
15. **Thiboutot, S., G. Ampleman, A. Hamel, J.M. Ballard, R. Martel, R. Lefebvre, and S. Downe** (2003) Research on the Environmental Conditions of Groundwater and Surface Water Prevailing in the Training Area at CFB Gagetown, New Brunswick, DRDC Valcartier TR-2003-016, Defence Research and Development Canada-Valcartier, Quebec, UNCLASSIFIED.
16. **Thiboutot, S., G. Ampleman, J. Lewis, D. Faucher, A. Marois, R. Martel, J.M. Ballard, S. Downe T. Jenkins, and A. Hewitt** (2003) Environmental Conditions of Surface Soils and Biomass Prevailing in the Training Area at CFB Gagetown, New-Brunswick, TR-2003-152, Defence Research and Development Canada-Valcartier, Quebec, UNCLASSIFIED.

17. **Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, and Major E. Wahlgren** (2001) Characterization of Explosives Contamination at Military Firing Ranges, ERDC Technical Report TR-01-05, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
18. **Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lynch, T.A. Ranney, J.A. Stark, M.E. Walsh, J. Lewis, C.A. Hayes, J.E. Mirecki, A.D. Hewitt, N. Perron, J. Clausen, and J.J. Delfino** (2002) Distribution and Fate of Energetics on DoD Test and Training Ranges: Interim Report 2, Technical Report ERDC TR-02-8, U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS.
19. **Pennington, J.C., T.F. Jenkins, G. Ampleman, S. Thiboutot, J.M. Brannon, J. Lewis, J.E. Delaney, J. Clausen, A.D. Hewitt, M.A. Hollander, C.A. Hayes, J.A. Stark, A. Marois, S. Brochu, H.Q. Dinh, D. Lambert, R. Martel, P. Brousseau, N.M. Perron, R. Lefebvre, W. Davis, T.A. Ranney, C. Gauthier, S. Taylor, and J.M. Ballard** (2003) Distribution and Fate of Energetics on DoD Test and Training Ranges: Report 3, ERDC TR-03-02, U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS.
20. **Hewitt, A.D., T.F. Jenkins, T.A. Ranney, D. Lambert, and N. Perron** (2004) Characterization of Explosives Residues at Military Firing Ranges: Schofield Barracks and Pohakuloa Training Area, Chapter 3. In Pennington J.C., et al., Distribution and Fate of Energetics on DoD Test and Training Ranges: Report 4, ERDC TR-04-4 ERDC Technical Report, Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS.
21. **Jenkins, T.F., C.L. Grant, G.S. Brar, P.G. Thorne, P.W. Schumacher, and T.A. Ranney** (1997a) Assessment of Sampling Error Associated with the Collection and Analysis of Soil Samples at Explosives Contaminated Sites. *Field Analytical Chemistry and Technology*, 1: 151–163.
22. **Jenkins, T.F., M.E. Walsh, P.G. Thorne, P.H Miyares, T.A. Ranney, C.L. Grant, and J. Esparza** (1998) Site Characterization for Explosives Contamination at a Military Firing Range Impact Area, Special Report 98-9, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

23. **Jenkins, T.F., C.L. Grant, M.E. Walsh, P.G. Thorne, S. Thiboutot, G. Ampleman, and T.A. Ranney** (1999) Coping with Spatial Heterogeneity Effects on Sampling and Analysis at an HMX—Contaminated Antitank Firing Range. *Field Analytical Chemistry and Technology* 3(1): 19–28.
24. **Hewitt, A.D., and M.E. Walsh** (2003) On-Site Processing and Subsampling of Surface Soils Samples for the Analysis of Explosives, ERDC/CRREL TR-03-14, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
25. **Walsh, M.E., C.M. Collins, A.D. Hewitt, M.R. Walsh, T.F. Jenkins, J. Stark, A. Gelvin, T.S. Douglas, N. Perron, D. Lambert, R. Bailey, K. Myers** (2004) Range Characterization Studies at Donnelly Training Area, Alaska: 2001 and 2002. ERDC/CRREL TR-04-3, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
26. **Thiboutot, S., G. Ampleman, A. Marois, A. Gagnon, M. Bouchard, A. Hewitt, T.F. Jenkins, M. Walsh, K. Bjella, C. Ramsey, and T.A. Ranney** (2004) Environmental Conditions of Surface Soils, CFB Gagetown Training Area: Delineation of the Presence of Munitions Related Residues (Phase III, Final Report), DRDC Valcartier TR 2004-205.
27. **Jenkins, T.F., J.C. Pennington, T.A. Ranney, T.E. Berry, Jr., P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, L.V. Parker, C.A. Hayes, Major E. Wahlgren** (2001) Characterization of Explosives Contamination at Military Firing Ranges, ERDC Technical Report TR-01-05, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
28. **Walsh, M.E., C.M. Collins, C.H. Racine, T.F. Jenkins, A.B. Gelvin, and T.A. Ranney** (2001) Sampling for Explosives Residues at Fort Greely, Alaska, Reconnaissance Visit July 2000, ERDC/CRREL TR-01-15, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
29. **Jenkins, T.F., A.D. Hewitt, C.L. Grant, S. Thiboutot, G. Ampleman, M.E. Walsh, T.A. Ranney, C.A. Ramsey, A.J. Palazzo, and J.C. Pennington** (2006) Identity and Distribution of Residues of Energetic Compounds at Army Live-Fire Training Ranges, *Chemosphere*, 63, 1280; Jenkins T.F., et al. (2005) Identity and Distribution of Residues of Energetic Compounds at Military Live-Fire Training Ranges, ERDC TR-05-10, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.

30. **Dubé, P., S. Thiboutot, G. Ampleman, A. Marois, and M. Bouchard** (2006) Preliminary Assessment of the Dispersion of Propellant Residues from the Static Live Firing of 105-mm Howitzer, DRDC Valcartier TM 2005-284.
31. **Walsh, M.R., S. Taylor, M.E. Walsh, S. Bigl, K. Bjella, T. Douglas, A.B. Gelvin, D. Lambert, N.M. Perron, and S.P. Saari** (2005) Residues from Live Fire Detonation of 155-mm Howitzer Rounds, ERDC/CRREL TR 05-14, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
32. **Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari** (2006) Energetic Residues Deposition from 60-mm and 81-mm Mortars, ERDC/CRREL TR 06-10, U.S. Army Engineer Research and Development Center, Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
33. **Expro Chemical Products Inc.** (1987) Description sheet of M1 propellant, lot PCE87M-2019.
34. **Ampleman, G., S. Thiboutot, A. Gagnon, A. Marois, R. Martel, and R. Lefebvre** (1998) Study of the Impacts of OB/OD Activity on Soils and Groundwater at the Destruction Area in CFAD Dundurn, DREV R-9827, UNCLASSIFIED.
35. **Thiboutot, S., G. Ampleman, A. Gagnon, A. Marois, T.F. Jenkins, M.E. Walsh, P.G. Thorne, and T.A. Ranney** (1998) Characterization of Antitank Firing Ranges at CFB Valcartier, WATC Wainwright and CFAD Dundurn, DREV R-9809, UNCLASSIFIED.
36. **Jenkins, T.F., M.E. Walsh, P.G. Thorne, P.H Miyares, T.A. Ranney, C.L. Grant, and J. Esparza** (1998) Site Characterization for Explosives Contamination at a Military Firing Range Impact Area, CRREL Special Report 98-9, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
37. **Brannon, J.M., T.F. Jenkins, L.V. Parker, P. Deliman, J.A. Gerald, C. Ruiz, B. Porter, and W.M. Davis** (2000) Procedures for Determining Integrity of UXO and Explosives Soil Contamination at Firing Ranges, Technical Report ERDC TR-00-4 (ERDC/CRREL MP-01-5604), U.S. Army Engineer Research and Engineering Center, Vicksburg, MS.
38. **Fellows, R.S., S.D. Harvey, and D.A. Cataldo** (1992) An Evaluation of the Environmental Fate and Behaviour of Munitions Material (TNT Metabolites) in Soil and Plant System, Contract DE-AC06-76RLO 1830.

39. **Selim, H.M., and I.K. Iskandar** (1994) Sorption-Desorption and Transport of TNT and RDX in Soils, CRREL Report AD-A-285-570, U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, New Hampshire.
40. **Cragin, J.H., D.C. Leggett, B.T. Foley, and P.W. Schumacher** (1985) TNT, RDX, and HMX Explosives in Soils and Sediments, Analysis Techniques and Drying Losses, U.S. Army Toxic and Hazardous Materials Agency, Report No. AMX-TH-TE-FR-85038, Aberdeen Proving Ground, MD.
41. **Pennington, J.C., T.F. Jenkins, J.M. Brannon, J. Lynch, T.A. Ranney, T.E. Berry, Jr., C.A. Hayes, P.H. Miyares, M.E. Walsh, A.D. Hewitt, N. Perron, and J.J. Delfino** (2001) Distribution and Fate of Energetics on DoD Test and Training Tangents: Interim Report 1, Technical Report ERDC TR-01-13, U.S. Army Engineer Research and Development Center, Vicksburg, MS.
42. <http://www.epa.gov/epaoswer/hazwaste/test/pdfs/8330.pdf>
43. <http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA200Met11.pdf>
44. **Canadian Forces Technical Order** (CFTO), Ammunition for 105 MM Howitzer, C-74-315-H00/TA-000.
45. **Thiboutot, S., G. Ampleman, R. Martel, D. Paradis, and R. Lefebvre** (2001) Environmental Characterization of Canadian Forces Base Shilo Training Area (Battleruns) Following GATES Closure, DREV TR 2001-126, UNCLASSIFIED.
46. **Ampleman, G., A. Hamel, J.M. Ballard, R. Martel, R. Lefebvre, and S. Downe** (2003) Research on the Environmental Conditions of Groundwater and Surface Water Prevailing in the Training Area at CFB Gagetown, New Brunswick, DRDC Valcartier TR-2003-016, Defence Research and Development Canada-Valcartier, Quebec, UNCLASSIFIED.

## **5 Transport of Nitroglycerin, Nitroguanidine and Diphenylamine in Soils**

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### **Introduction**

#### *Background*

Tests of propellant fibers conducted by Dr. Thomas F. Jenkins near a firing point on an Alaskan range during execution of SERDP Project ER-1155 suggested that the propellant constituents are not readily depleted from the nitrocellulose (NC) matrix (Pennington et al. 2003). The rate of release of propellant constituents from NC formulations under environmental conditions is unknown. Constituent release should be defined in terms of temperature, surface area, and mixing rate. A study in our laboratory under the Corps of Engineers Environmental Quality Technology Program, “Enhanced Fate and Transport of Propellants, Smokes, and Illuminants,” with leveraged funding from SERDP project ER-1155 (formerly CP-1155), determined solubilities of selected propellant components (diphenylamine, N-nitrosodiphenylamine, and ethyl centralite) in stirred reactors. Solubilities were temperature-dependent and ranged from 10 to 60 ppm (Brannon et al. 2004). Mirecki et al. (2006) addressed dissolution from propellant formulations, M1, M9, M10, and M30 in stirred reactors (Table 5-1). However, since these data cannot take into account subsequent transport of dissolved constituents through the soil, column transport studies were also conducted.

Propellants are classified single-, double-, and triple-base depending on presence of nitrocellulose (NC) only; nitrocellulose and nitroglycerin (NG); or nitrocellulose, nitroglycerine, and nitroguanidine (NQ). Propellants used in firing heavy artillery include M1 (single-base), M9 (double-base), M10 (single-base), and M30 (triple-base) (Table 5-1). In addition to the active propellants, nitrocellulose, nitroglycerin, and nitroguanidine, propellant formulations contain stabilizers of nitrocellulose, which has an inherently poor stability. These include dinitrotoluenes (in single-base propellant formulations), diphenylamine (in single-base propellants only, since it is incompatible with nitroglycerin), and ethyl centralite (in single-, double-, and triple-base propellants). Plasticizers, e.g., dibutyl phthalate, are added to decrease brittleness. Lead or bismuth compounds are added to prevent copper residue from accumulating from the gun barrel

rifling. Potassium nitrate, potassium sulfate, and/or cryolite are added to reduce the intensity of the muzzle flash. Pellets may or may not be graphite-coated to prevent grains from sticking together and to prevent static electricity from causing undesired ignitions. Cylindrical propellants, e.g., M1, are perforated by typically one or seven holes running the length of the cylinder and measuring 0.02 to 0.15 cm (0.01 to 0.06 inches) in diameter. These perforations stabilize the burn rate of the propellant.

**Table 5-1. Composition of selected propellant formulations.**

<b>Component</b>	<b>Chemical Abstracts Service (CAS) Number</b>	<b>Formulation (%)</b>			
		<b>M1</b>	<b>M9</b>	<b>M10</b>	<b>M30</b>
Nitrocellulose	9004-70-0	85.00	57.75	98.00	28.00
Nitroglycerin	55-63-0		40.00		22.50
Nitroguanidine	556-88-7				47.70
Dinitrotoluene	Mix of two isomers <sup>1</sup>	10.00			
Diphenylamine	122-39-4	1.00 <sup>2</sup>		1.00	
Ethyl centralite <sup>3</sup>	85-98-3		0.75		1.50
Dibutyl phthalate	84-74-2	5.00			
Lead carbonate	589-63-0	1.00 <sup>2</sup>			
Potassium nitrate	7757-79-1		1.50		
Potassium sulfate	7778-80-5			1.00	
Cryolite <sup>4</sup>	15096-52-3				0.30
Graphite	12069-32-8		0.40 max		

<sup>1</sup> 2,4-dinitrotoluene, CAS 121-14-2, and 2,6-dinitrotoluene, CAS 606-20-2; relative amounts vary.

<sup>2</sup> Component added after the propellant was mixed. Lead compounds are being phased out because of lead toxicity.

<sup>3</sup> N,N'-diethyl-N,N'-diphenylurea.

<sup>4</sup> Sodium aluminum fluoride.

Previous research defined partition (adsorption) coefficients ( $k_d$ ), soil persistence (half-life), and degradation/transformation rates ( $\mu_w$ ) for a suite of explosives, their degradation/transformation products, and a few propellant components, specifically nitroguanidine, diphenylamine, and N-nitroso-

diphenylamine (Pennington et al. 2004). These studies were conducted in stirred reactors or shake tests rather than in columns. Results of these previous studies will be compared with results of column studies when applicable.

### ***Objectives***

Objectives of the study include the following:

- (1) To describe transport of solution phase propellant constituents of selected propellant formulations.
- (2) To develop process descriptors (soil-to-water partition coefficients, half-life in soils, and transport rates), which are needed to model transport and to assess environmental and public health risks.

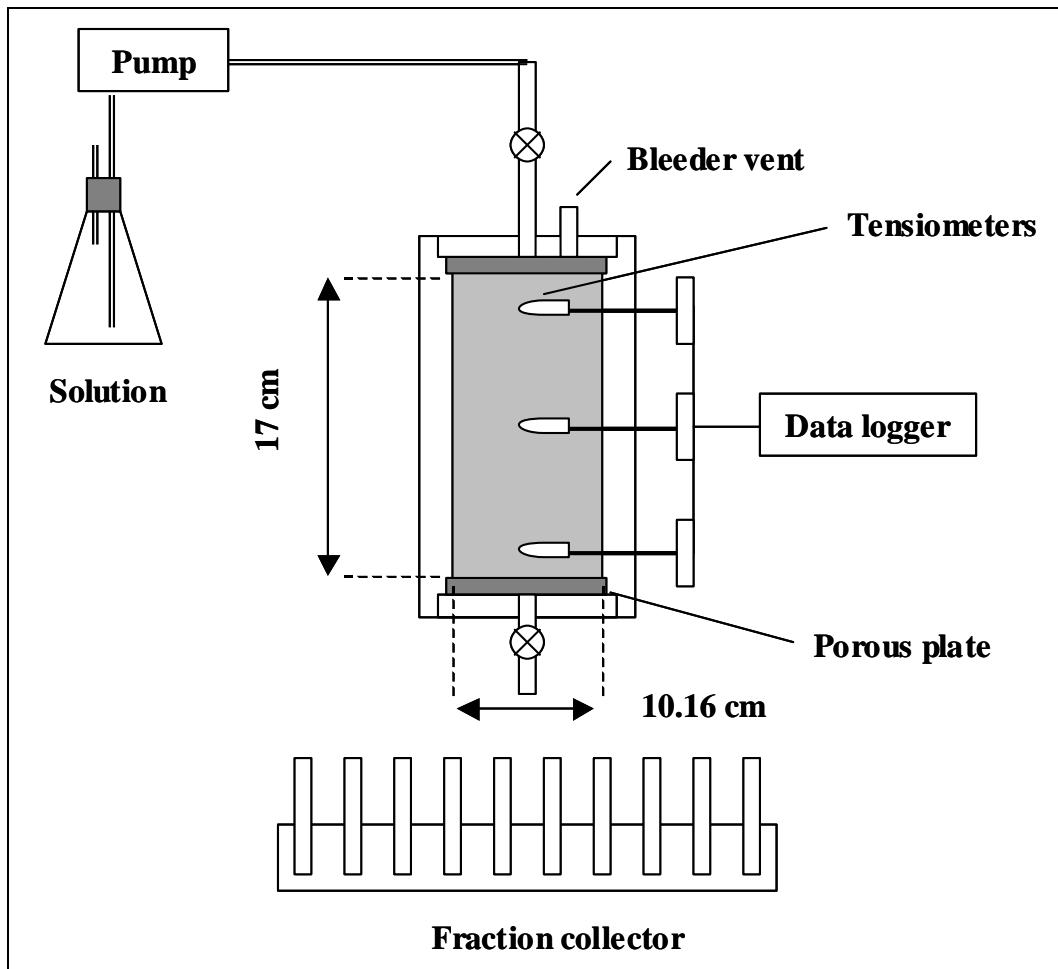
### ***Approach***

A series of column-leaching experiments were conducted for propellant constituents (NG, NQ, and DPA). Individual propellants constituents in solution were studied in saturated column experiments to define breakthrough curves in two soils having different transport potential. Interrupted flow experiments, along with a conservative tracer ( $^3\text{H}_2\text{O}$ ), were used to distinguish between physical and chemical non-equilibrium processes. Mass balance for each experiment was used to determine whether constituents were transformed and/or degraded to other products. An existing analytical model, HYDRUS-1D (Šimunek et al. 2005), was used to describe the observed breakthrough curves. Transport parameters were determined by fitting of the transport equations to the experimental breakthrough curves (Šimunek et al. 2002). Resulting transport parameters are suitable for incorporation into environmental and human health risk assessment models. In future studies, leaching experiments will be conducted for two solid-phase formulations of propellants.

### **Materials and Methods**

A series of leaching experiments was conducted in stainless-steel cylindrical columns measuring 10.16 cm in diameter by 17.00 cm high (Fig. 5-1). The top and bottom of each column was fitted with Media Grade 100 porous stainless-steel plates (Mott Corporation, Farmington, Connecticut). Stainless-steel top caps contained a solution input valve and bleeder valve; bottom caps contained a solution export valve. Propellant solutions were pumped into the column through the input valve by an attached low-flow peristaltic pump (Fisher Scientific, Houston, Texas) calibrated to a flow rate of  $1.18 \text{ mL min}^{-1}$  ( $0.87 \text{ cm h}^{-1}$  flux).

Outflow samples were collected into 40-mL amber glass vials using an automatic Universal Fraction Collector (Eldex Laboratories, Inc., Napa, California).



**Figure 5-1. Schematic of flow-through column system based on flux-controlled system by Wilson et al. (1998).**

The columns were packed with Plymouth sand (mesic, coated Typic Quartzipsammments) or Adler silt (coarse-silty, mixed, superactive, thermic Fluvaquentic Eutrudepts) (Table 5-2). Plymouth sand was collected at the Massachusetts Military Reservation in Camp Edwards, Massachusetts, and Adler silt was collected at the U.S. Army Engineer Research and Development Center in Vicksburg, Mississippi. Both soils were air-dried, ground, and passed through a 2-mm sieve.

<b>Table 5-2. Physical and chemical properties of test soils.</b>						
	CEC, <sup>1</sup> (cmol <sub>c</sub> kg <sup>-1</sup> )	OM, <sup>2</sup> (g kg <sup>-1</sup> )	Particle Size (g kg <sup>-1</sup> )			pH
			Sand	Silt	Clay	
Adler Silt	16.6	5	125	833	42	7.9
Plymouth Sand	4.4	8.5	933	58	8	5.2

<sup>1</sup> Cation Exchange Capacity  
<sup>2</sup> Organic matter

Columns were saturated with a 0.005M CaBr<sub>2</sub> solution prior to introduction of propellant solutions. Once saturated, CaBr<sub>2</sub> solution was replaced with a solution containing the propellant constituents, NQ, NG, or DPA. Nitroguanidine (Aldrich, Milwaukee, Wisconsin) and DPA (Aldrich, Milwaukee, Wisconsin) solutions were prepared at a target concentration of 20 mg L<sup>-1</sup>. Nitroglycerin (Restek, Bellefonte, Pennsylvania) solutions also were prepared at 20 mg L<sup>-1</sup>, but were amended with 0.20 µg mL<sup>-1</sup> (73,721.3 dpm mL<sup>-1</sup> or 0.03 µCi mL<sup>-1</sup>) uniformly labeled <sup>14</sup>C-NG (specific activity of 53.5 mCi mmol<sup>-1</sup> and radiochemical purity of 99%, PerkinElmer Life Sciences, Inc., Boston, Massachusetts). All propellant solutions were prepared with 0.004 µg mL<sup>-1</sup> <sup>3</sup>H<sub>2</sub>O (1000 dpm mL<sup>-1</sup>, or 0.0005 µCi mL<sup>-1</sup>, specific activity 2.18 mCi mmol<sup>-1</sup>). After five to seven pore volumes of propellant solution were passed through, flow was switched back to the CaBr<sub>2</sub> solution for another five to six pore volumes. Two experiments were conducted for each soil and compound: a continuous flow experiment and an interrupted flow experiment, in which pumping of solution was stopped for 24 hours to allow propellants to equilibrate with the soil.

Aqueous and soil samples of NQ and NG treatments were analyzed using high-performance liquid chromatography (HPLC). NG samples were analyzed using SW846 Method 8332 (U.S. Environmental Protection Agency 1996a), with detection limits of 0.050 mg L<sup>-1</sup> in water and 0.250 mg kg<sup>-1</sup> in soils. NQ samples were analyzed using the method described in USACE Special Report 89-35 (Walsh 1989), with detection limits of 0.050 mg L<sup>-1</sup> in water and 0.250 mg kg<sup>-1</sup> in soils. DPA aqueous and soil samples were analyzed by gas chromatography-nitrogen phosphorus detector (GC-NPD) using SW846 Method 8070A, with detection limits of 0.025 mg L<sup>-1</sup> water and 0.030 mg kg<sup>-1</sup> soils (U.S. Environmental Protection Agency 1996b). Aqueous <sup>14</sup>C-NG samples were counted on a Tricarb 2500TR Liquid Scintillation Counter (Packard Co., Meriden, CT). <sup>14</sup>C-NG soil samples were combusted using a Model 307 Sample Oxidizer (Packard Co., Meriden, Connecticut), and the CO<sub>2</sub> was trapped and counted by liquid scintillation counting.

## Results and Discussion

### *Conservative tracer*

In all experiments, the input pulse of propellant was accompanied by concurrent input of a conservative tracer, tritiated water. Hollow triangles on Figures 5-2 through 5-7 represent measured values for outflow concentrations of the  $^3\text{H}_2\text{O}$  (labeled on figures as “measured water”). Breakthrough curves were analyzed using HYDRUS-1D inverse solution option and plotted on a time basis to accurately present interrupted flow experiments. Curves simulated by HYDRUS-1D are represented by dashed lines. Fitting resulted in  $R^2$  values ranging from 0.965 to 0.987.

Breakthrough of the conservative tracer was used to determine pore volume for the columns and longitudinal dispersivity,  $\lambda$ . Pore volume averaged 738 mL for Adler and 417 mL for Plymouth soil. Dispersivity was larger for the coarser Plymouth soil (0.59–1.01 cm) than for the finer Adler soil (0.11–0.30 cm) (Table 5-3), but generally small as expected for short repacked columns.

Interrupted flow experiments were used to evaluate the extent of physical non-equilibrium. Outflow concentrations of  $^3\text{H}_2\text{O}$  resumed at similar values after the flow interruption, indicating that no, or only limited, physical non-equilibrium occurred. Mass balance calculations indicated recovery of all tritiated water (average of 12 experiments:  $106 \pm 7\%$ ) (Table 5-4). Outflow concentrations of  $^3\text{H}_2\text{O}$  in excess of inflow concentrations in some experiments can be explained by scatter in data that influenced estimates of inflow concentration. This does not affect determined water flow parameters.

### *Nitroglycerin*

Solid diamonds represent measured values and the solid line in Figures 5-2 and 5-3 was generated for the  $^{14}\text{C}$ -NG radiotracer for the two soils with and without interrupted flow. In Adler soil,  $^{14}\text{C}$ -NG breakthrough was observed only slightly later than the conservative tracer, indicating limited adsorption to the soil. In Plymouth soil, breakthrough was delayed to a greater extent, probably due to the larger OM content of Plymouth soil (Table 5-2). Accordingly, average  $k_d$  values determined from the curves were larger for Plymouth ( $0.17 \text{ cm}^3 \text{ g}^{-1}$ ) than for Adler ( $0.08 \text{ cm}^3 \text{ g}^{-1}$ ) soil (Table 5-3). Previous work with Plymouth soil yielded a  $k_d$  of  $2 \text{ cm}^3 \text{ g}^{-1}$  (Spielert et al. 2002). This work also showed that the desorption  $k_d$  was  $71 \text{ cm}^3 \text{ g}^{-1}$ , an order of magnitude higher than the sorption  $k_d$ .

**Table 5-3. Solute transport parameters obtained by HYDRUS-1D for saturated flow experiments with  $^3\text{H}_2\text{O}$ ,  $^{14}\text{C}$ -NG, NQ, and DPA in Adler and Plymouth soils.**

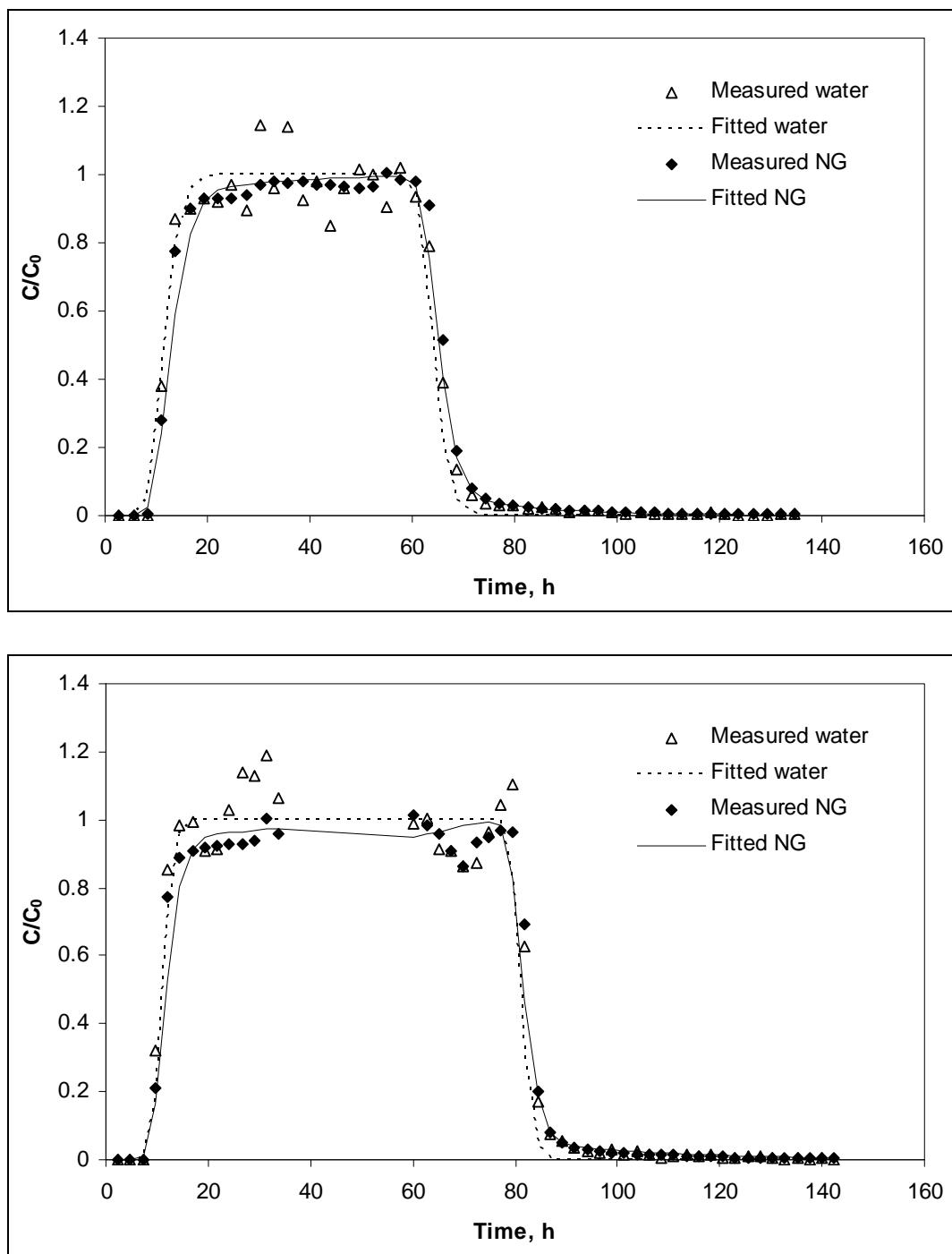
		Water flow parameters		Solute transport parameters				
		$\lambda^{1,2}$ (cm)	$R^2$	$f$	$k_d$ $\text{cm}^3 \text{g}^{-1}$	$\mu_w$ ( $\text{h}^{-1}$ )	$\omega$ ( $\text{h}^{-1}$ )	$R^2$
$^{14}\text{C}$ -NG	Adler	$0.30 \pm 0.13^3$	0.974	$0.43 \pm 0.16$	$0.08 \pm 0.00$	NA	$0.05 \pm 0.01$	0.987
	Plymouth	$0.59 \pm 0.12$	0.965	$0.43 \pm 0.14$	$0.17 \pm 0.03$	$0.008 \pm 0.004$	$0.17 \pm 0.06$	0.997
NQ	Adler	$0.20 \pm 0.03$	0.968	NA <sup>4</sup>	$0.03 \pm 0.01^5$	NA	NA	0.941
	Plymouth	$0.87 \pm 0.23$	0.987	$0.41 \pm 0.23$	$0.14 \pm 0.10$	NA	$0.05 \pm 0.06$	0.987
DPA	Adler	$0.11 \pm 0.04$	0.985	NA	$2.26 \pm 0.21$	$0.011 \pm 0.007$	NA	0.966
	Plymouth	$1.01 \pm 0.19$	0.970	NA	$1.94 \pm 0.26$	$0.014 \pm 0.001$	NA	0.952

<sup>1</sup>  $\lambda$  was estimated from  $^3\text{H}_2\text{O}$  breakthrough, while  $f$ ,  $k_d$ ,  $\mu_w$ , and  $\omega$  were estimated from propellant breakthrough curves.  
<sup>2</sup>  $\lambda$  = longitudinal dispersivity;  $f$  = fraction of sites with instantaneous adsorption;  $k_d$  = adsorption coefficient;  $\mu_w$  = first-order rate coefficient for dissolved phase, degradation rate (for  $^{14}\text{C}$  radiotracer experiments indicated irreversible attenuation);  $\omega$  = first-order rate coefficient for two-site non-equilibrium adsorption.  
<sup>3</sup> means  $\pm$  standard deviation  
<sup>4</sup> Not applicable  
<sup>5</sup> Value was not significantly different from zero.

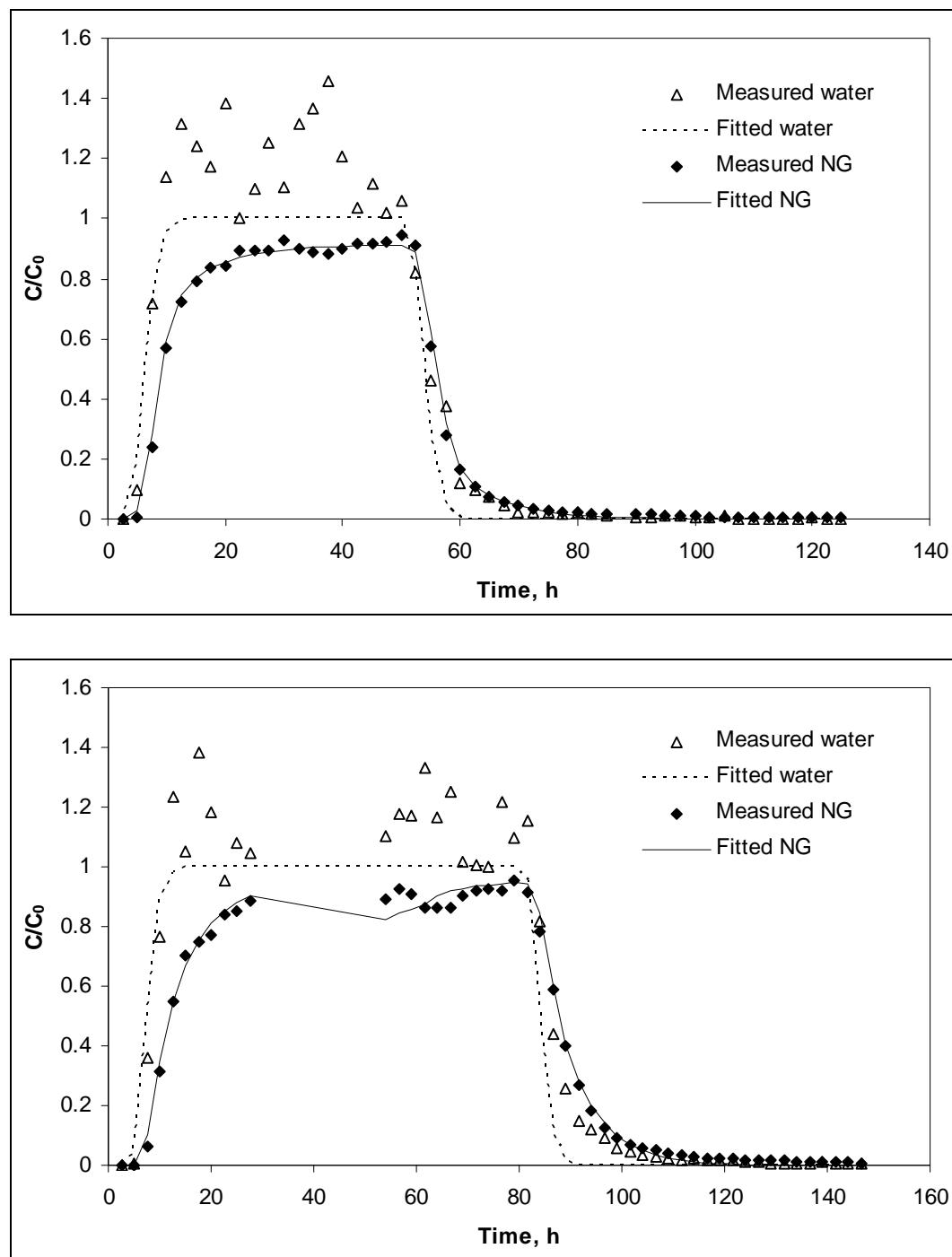
**Table 5-4. Percent recovery of solutes in outflow in the column transport experiments with  $^3\text{H}_2\text{O}$ ,  $^{14}\text{C}$ -NG, NQ, and DPA in Adler and Plymouth soils.**

Soil	Treatment	$^3\text{H}_2\text{O}$	$^{14}\text{C}$ -NG	NQ	DPA
Adler	NG	100	101	NA	NA
	NG IF <sup>1</sup>	108	102	NA	NA
Plymouth	NG	119	89	NA	NA
	NG IF	117	91	NA	NA
Adler	NQ	106	NA <sup>2</sup>	99	NA
	NQ IF	102	NA	101	NA
Plymouth	NQ	99	NA	102	NA
	NQ IF	97	NA	97	NA
Adler	DPA <sup>2</sup>	108	NA	NA	pending
	DPA IF	105	NA	NA	pending
Plymouth	DPA	102	NA	NA	pending
	DPA IF	103	NA	NA	pending

<sup>1</sup> IF = interrupted flow  
<sup>2</sup> Not applicable



**Figure 5-2. Breakthrough curves for nitroglycerin (NG) and tritiated water in Adler soil for continuous (top) and interrupted (bottom) flow experiments.**



**Figure 5-3. Breakthrough curves for nitroglycerin (NG) and tritiated water in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments.**

For Adler soil, sorption was reversible; recovery of  $^{14}\text{C}$ -NG varied between 101 and 102% (Table 5-4). The degradation rate of NG was not significantly different from zero when modeled by HYDRUS-1D (Table 5-3). Generated values for degradation rate would result in a very long half-life (62 years). For Plymouth soil, some degradation was observed, as indicated by a lower  $^{14}\text{C}$ -NG recovery in outflow (89–91%) and a significant transformation rate coefficient ( $\mu_w = 0.008 \pm 0.004 \text{ h}^{-1}$ ). Calculated half-life was 88.1 h. Breakthrough curves also indicated that the outflow concentrations approached inflow concentrations for Adler soil, but were less than inflow for Plymouth soil. It is likely that mineralization to  $\text{CO}_2$  contributed to NG fate in Plymouth soil, because combustion of soil samples and trapping of  $^{14}\text{C}$  resulted in recovery of only  $2.3 \pm 0.2\%$  of  $^{14}\text{C}$ -NG. Mineralization of NG in soil suspensions was previously observed by Yost (2004). Recovery of  $^{14}\text{C}$ -NG in Adler soil was  $0.9 \pm 0.2\%$ .

HPLC analysis of soil samples at the end of experiment indicated that no NG was left in the column (Table 5-5). Several samples of outflow were also analyzed for NG by HPLC. Outflow recoveries of NG, measured by HPLC, were similar to  $^{14}\text{C}$ -NG recoveries in Plymouth soil, while in Adler soil recoveries of NG were 25% smaller, indicating that while no degradation was indicated by  $^{14}\text{C}$ -NG, transformation of NG was occurring.

The asymmetric shape of the breakthrough curves for both soils and results of HYDRUS-1D simulations suggest rate-controlled adsorption and desorption. An estimated 43% of adsorption sites exhibited kinetic adsorption, with the rate of exchange in the  $0.05$  to  $0.17 \text{ h}^{-1}$  range (Table 5-3). However, there was no consistent decrease in concentration following flow interruption that indicates chemical non-equilibrium or degradation.

Nitroglycerin exhibited less retardation in studied soils than was reported in the previous literature;  $k_d$  values for  $^{14}\text{C}$ -NG determined from HYDRUS-1D (Table 5-3) were smaller than values determined in batch experiments for similar soils and sediments (Pennington et al. 2003). Degradation rates were in the same range as reported by Pennington et al. (2003) for low carbon soils ( $0.002$  to  $0.008 \text{ h}^{-1}$ ).

### *Nitroguanidine*

Nitroguanidine exhibited very little attenuation as indicated by a similarity between breakthrough curves of tritiated water and nitroguanidine (Fig. 5-4 and 5-5). Estimated degradation and adsorption coefficients were very small (Table 5-3). Degradation as estimated by HYDRUS-1D was non-significant for both soils. Calculated half-life was one month for Plymouth soil to 15 years in Adler soil. Adsorption was significant only for Plymouth soil. Somewhat greater

average  $k_{ds}$  for nitroguanidine in Plymouth soil ( $0.14 \text{ cm}^3 \text{ g}^{-1}$ ) can possibly be explained by its higher OM content (Table 5-2). Mass balance of NQ (Table 5-4) indicated complete recovery of propellant in both soils ( $100 \pm 1\%$  and  $100 \pm 4\%$  for Adler and Plymouth soils, respectively).

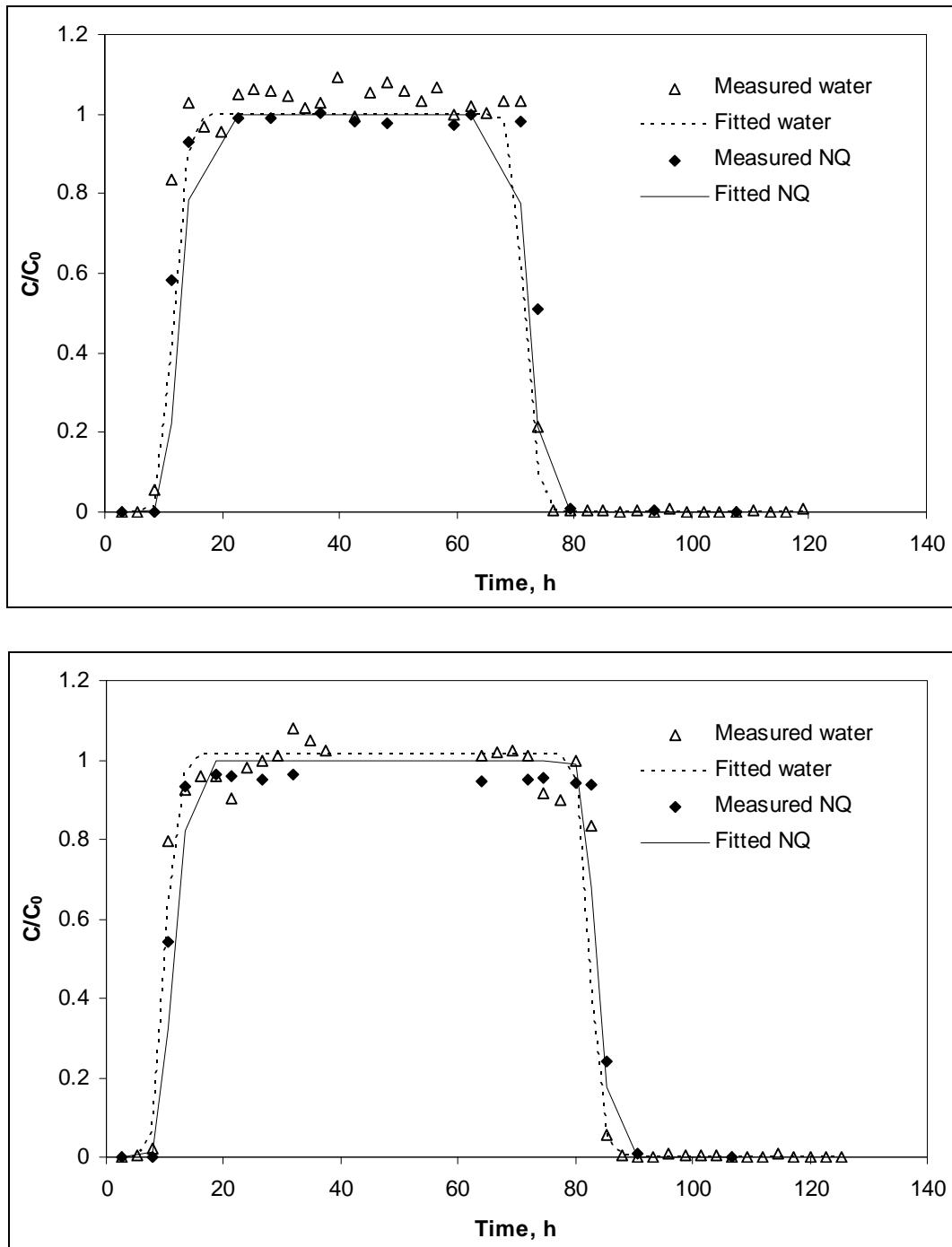
**Table 5-5. Soil concentrations of NG, NQ, and DPA ( $\text{mg kg}^{-1}$ ) at the end of the experiment in bottom (15–17 cm), middle (9–10 cm), and top layer (1–2 cm) of Adler and Plymouth soils.**

Soil/treatment	Sampling depth (cm)	NG ( $\text{mg kg}^{-1}$ )	NQ ( $\text{mg kg}^{-1}$ )	DPA ( $\text{mg kg}^{-1}$ )
Adler	15–17	<0.1	0.025 J	0.60
	9–10	<0.1	0.035 J	1.41
	1–2	<0.1	0.03 J	3.06
Adler IF	15–17	<0.1	0.03 J	0.83
	9–10	<0.1	0.045 J	0.59
	1–2	<0.1	0.045 J	2.80
Plymouth	15–17	<0.1	0.17 J	4.96
	9–10	<0.1	0.12 J	3.13
	1–2	<0.1	0.105 J	2.79
Plymouth IF	15–17	<0.1	0.145 J	4.77
	9–10	<0.1	0.125 J	2.13
	1–2	<0.1	0.135 J	3.04

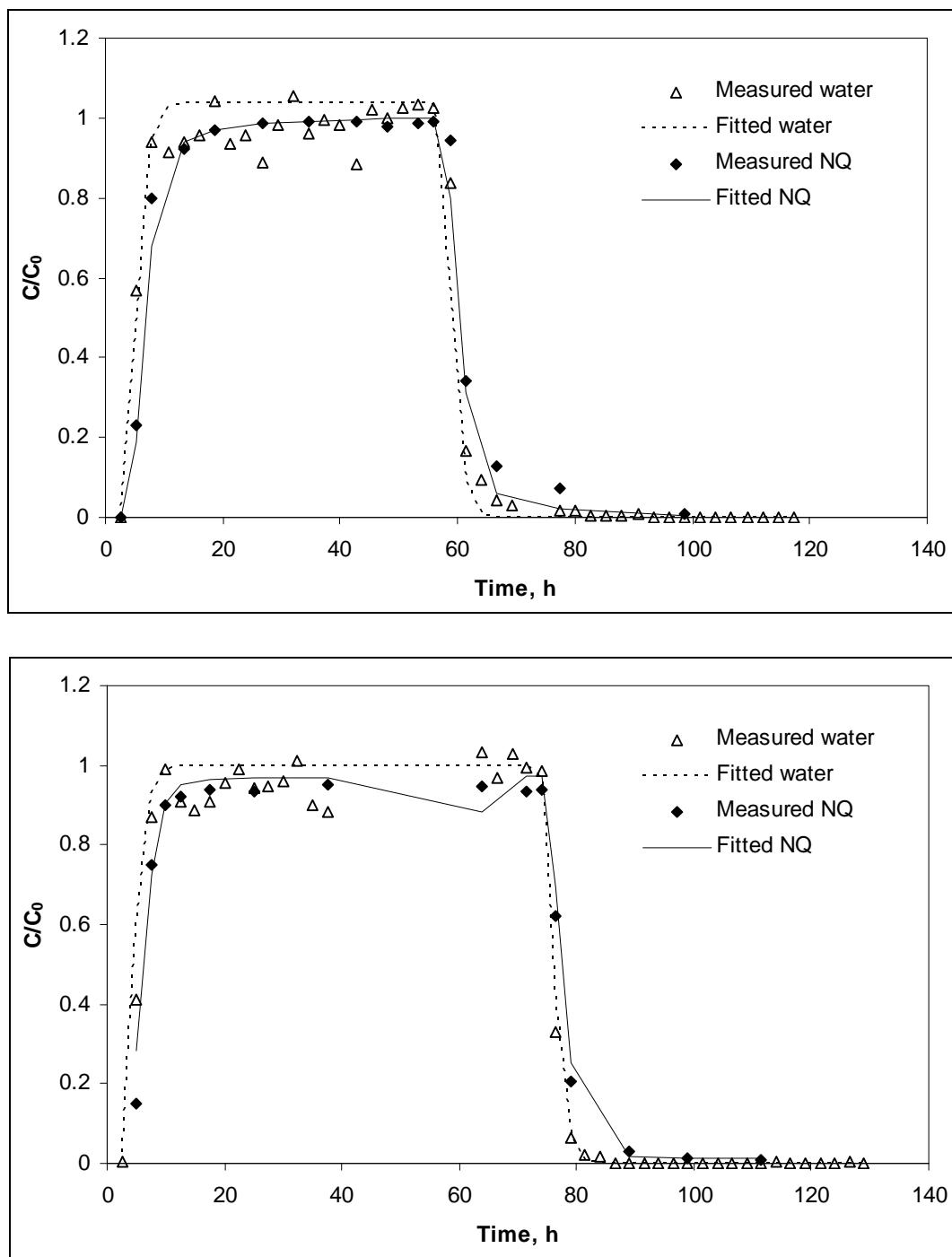
J = concentrations falling above the method detection limit, but below the laboratory reporting limit.

Low reactivity of NQ in soil observed in our experiments agrees with earlier studies by Haag et al. (1990) and by Pennington et al. (2004), who for similar soils also measured very small  $k_{ds}$  ( $0.15\text{--}0.26 \text{ cm}^3 \text{ g}^{-1}$ ) and no degradation of nitroguanidine. However, in reduced environments, degradation of nitroguanidine has been reported (Kaplan et al. 1982).

Limited non-equilibrium sorption was observed for Plymouth soil as illustrated by an asymmetric breakthrough curve (Fig. 5-5); however, outflow concentration did not decrease after flow interruption. Estimated values for kinetic sorption parameters ( $f$  and  $\omega$ ) in Adler soil were largely non-significant, and, therefore, were removed from the model (Table 5-3).



**Figure 5-4. Breakthrough curves for nitroguanidine (NQ) and tritiated water in Adler soil for continuous (top) and interrupted (bottom) flow experiments.**



**Figure 5-5. Breakthrough curves for nitroguanidine (NQ) and tritiated water in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments.**

### *Diphenylamine*

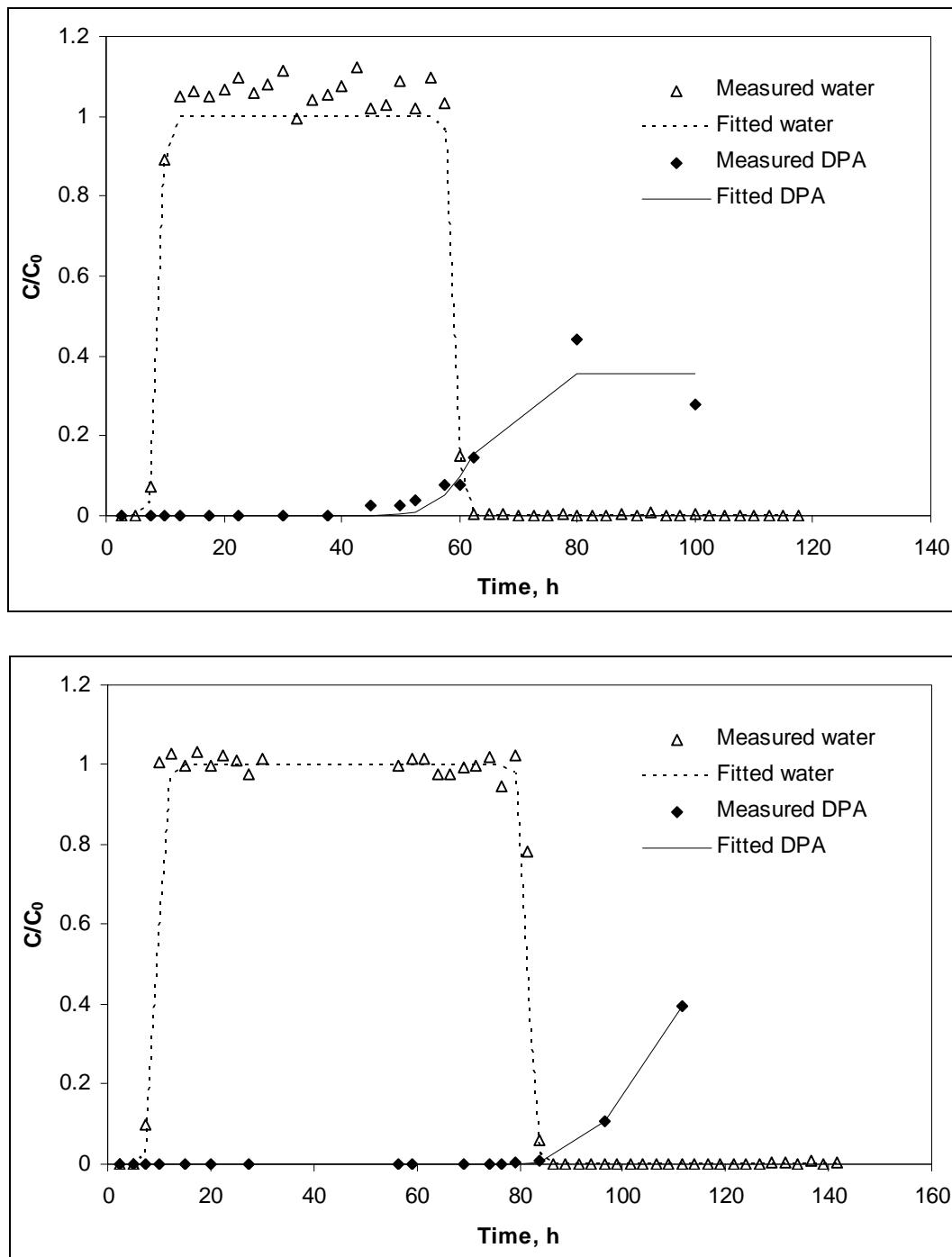
Unlike nitroglycerin and nitroguanidine, diphenylamine exhibited considerable retardation in column transport experiments (Fig. 5-6 and 5-7). Both adsorption and degradation were observed. Adsorption coefficients were  $2.26 \pm 0.21 \text{ cm}^3 \text{ g}^{-1}$  in Adler soil and  $1.94 \pm 0.26 \text{ cm}^3 \text{ g}^{-1}$  in Plymouth soil. These values are in agreement with values for similar soils ( $1.66$  and  $3.8 \text{ cm}^3 \text{ g}^{-1}$ ) (Pennington et al. 2004). Analysis of soil after completion of the experiments indicated that breakthrough was not complete (Table 5-5).

Degradation rates were  $0.011$  and  $0.014 \text{ h}^{-1}$  for Adler and Plymouth soils, respectively. These rates would result in half-lives of  $62.3$  and  $48.1 \text{ h}$ . These values are higher than values reported by Pennington et al. (2004). Mass balance data for diphenylamine are pending.

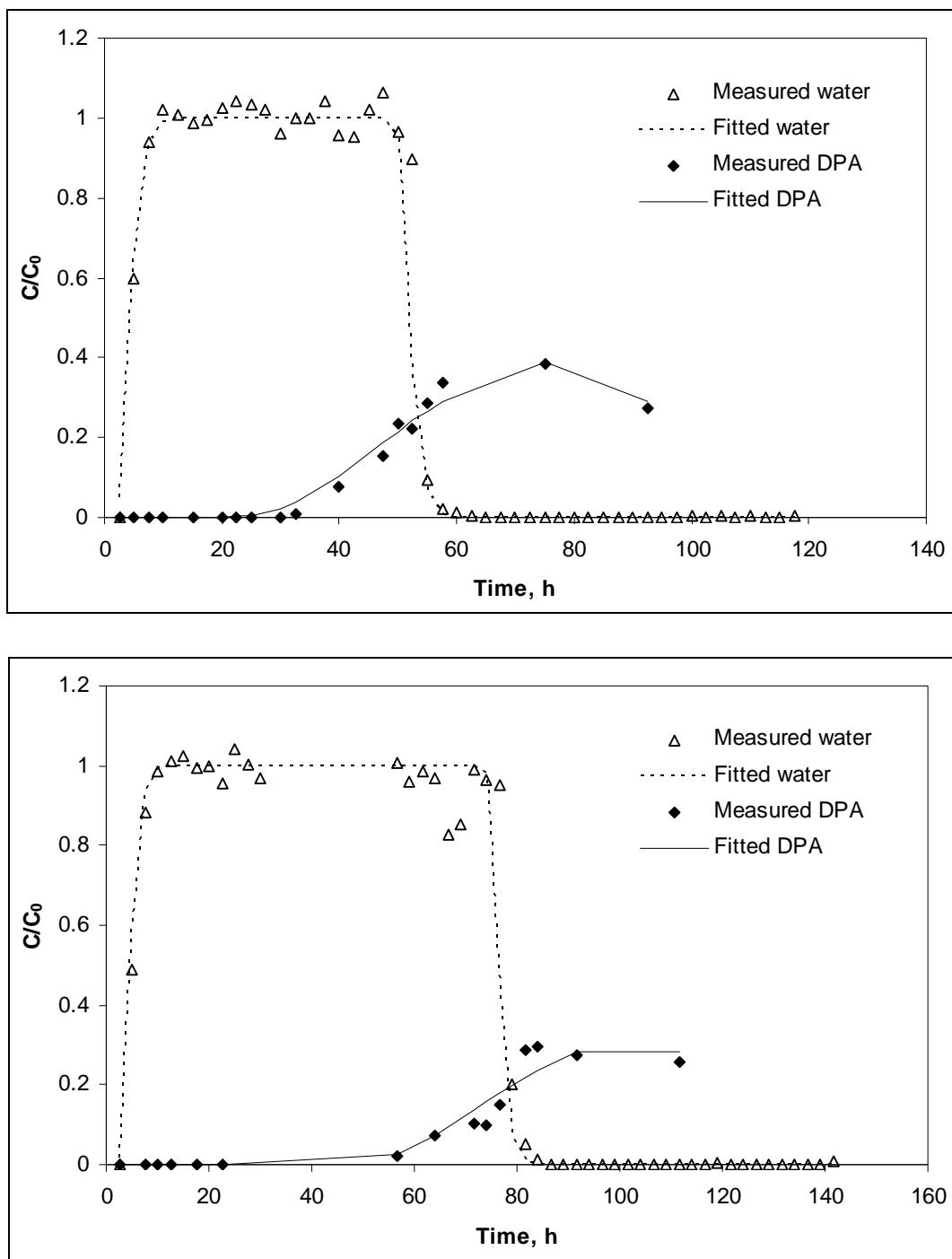
No degradation products of any of the propellant components were detected in outflow or soils.

### **Conclusions**

Nitroglycerin and nitroguanidine exhibited limited retardation and degradation in low OC soils, indicating potential for movement into groundwater.  $k_d$  values were less than  $0.2 \text{ cm}^3 \text{ g}^{-1}$ ;  $\mu_w$  was either not statistically different from zero or relatively small ( $0.008 \text{ h}^{-1}$  or half-life of  $88.1 \text{ h}$ ). Transport parameters for diphenylamine were as follows:  $k_d$  values were about  $2 \text{ cm}^3 \text{ g}^{-1}$ , retardation factors were 6 to 10;  $\mu_w$  was  $0.011$  to  $0.014 \text{ h}^{-1}$ , and half-life was  $48.1$  to  $62.3 \text{ h}$ . Diphenylamine exhibited both sorption and degradation, suggesting that it can be retained and/or degraded in the soil. Therefore, diphenylamine is less likely to migrate to groundwater than is nitroglycerin or nitroguanidine.



**Figure 5-6. Breakthrough curves for diphenylamine (DPA) and tritiated water in Adler soil for continuous (top) and interrupted (bottom) flow experiments.**



**Figure 5-7. Breakthrough curves for diphenylamine (DPA) and tritiated water in Plymouth soil for continuous (top) and interrupted (bottom) flow experiments.**

## References

**Brannon, J.M., C.B. Price, S.L. Yost, C. Hayes, J.E. Mirecki, and B. Porter** (2004) Fate and transport parameters for firing range residues. Chapter 9. Distribution and fate of energetics on DoD test and training ranges: Interim Report 4. ERDC TR-04-4. U. S. Army Engineer Research and Development Center, Vicksburg, MS.

**Haag, W.R., R. Spanggord, T. Mill, R.T. Podoll, T.-W. Chou, D.S. Tse, and J.C. Harper** (1990) Aquatic environmental fate of nitroguanidine. *Environmental Toxicology and Chemistry* 9: 1369–1367.

**Kaplan, D.L., J.H. Cornell, and A.M. Kaplan** (1982) Decomposition of nitroguanidine. *Environmental Science and Technology* 16: 488–492.

**Mirecki, J.E., B. Porter, and C.A. Weiss** (2006) Environmental transport and fate process descriptors for propellant compounds. ERDC TR-06-7. U.S. Army Engineer Research and Development Center, Vicksburg, MS.

**Pennington, J.C., J. Clausen, and T.F. Jenkins** (2003) Introduction, Chapter 1 Distribution and fate of energetics on DoD test and training ranges: Interim Report 3. ERDC TR-03-2. U.S. Army Engineer Research and Development Center, Environmental Laboratory, Vicksburg, MS.

**Pennington, J.C., T.F. Jenkins, G. Ampleman, and S. Thiboutot** (2004) Distribution and fate of energetics on DoD test and training ranges: Interim Report 4. Technical report TR-04-4-4. U. S. Army Engineer Research and Development Center.

**Šimunek, J., D. Jacques, J.W. Hopmans, M. Inoue, M. Flury, and M.T. van Genuchten** (2002) Solute transport during variably-saturated flow—Inverse methods, p. 1435–1449. In *Methods of Soil Analysis, Part I, Physical Methods, Third Edition*, J.H. Dane and G.C. Topp, eds. Madison, Wisconsin: SSSA.

**Šimunek, J., M.T. van Genuchten, and M. Šejna** (2005) The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably saturated media. Version 3.0. Department of Environmental Sciences, University of California Riverside, Riverside, CA.

**Speitel, G.E., H. Yamamoto, R.L. Autenrieth, and T. McDonald** (2002) *Laboratory Fate and Transport Studies of High Explosives at the Massachusetts Military Reservation*. Final Report. January 2002. Prepared for National Guard Bureau by the University of Texas at Austin and Texas A&M University.

**U.S. Environmental Protection Agency** (1996a) SW846 Method 8332. Nitroglycerine by high-performance liquid chromatography. Office of Solid Waste and Emergency Response, Washington, DC.

**U.S. Environmental Protection Agency** (1996b) SW846 Method 8070A. Nitrosoamines by gas chromatography. Office of Solid Waste and Emergency Response, Washington, DC.

**Walsh, M.E.** (1989) Analytical methods for determining nitroguanidine in soil and water. Special Report 89-35. U.S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

**Wilson, G.V., L. Yunsheng, H.M. Selim, M.E. Essington, and D.D. Tyler** (1998) Tillage and cover crop effects on saturated and unsaturated transport of fluometuron. *Soil Science Society of America Journal* 62: 46–55.

**Yost, S.** (2004) Effects of redox potential and pH on the fate of nitroglycerin in a surface and aquifer soil. M.S. Thesis. The Department of Environmental Studies, Louisiana State University, Baton Rouge, LA.

## **6 Dispersion of Ammonium Perchlorate Following the Static Firing of Mk58 Rocket Motors**

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### **Abstract**

Static firing of AIM-7 rocket motors was conducted in June 2006 at the DRDC Valcartier test site on CFB Valcartier to measure the environmental dispersion of ammonium perchlorate (AP) during normal burning conditions as part of SERDP ER-1481 (Strategic Environmental R&D Program—Environmental Restoration Project # 1481). The recent stringent threshold criterion for perchlorate in drinking water dictates that the sources of this contaminant must be better defined in order to minimize its further dispersion into the environment. It is thought that perchlorate-based solid rocket propellants burn completely in pressurized motors, but there are very few literature data to support this hypothesis. The AIM-7 Sparrow missile, which is propelled by an Mk58 AP-based motor, has been the main medium-range air-to-air missile used by both U.S. and Canadian fighter jets for many years. Fifteen Mk58 motors were obtained for this study from the Canadian inventory and were statically fired on a test bench to measure the residues that were expelled during combustion. The field setup to catch potential perchlorate particles was optimized by testing it prior to the burning of Mk58 motors. It was based on a combination of the use of aluminium witness plates and of aqueous traps located in the exhaust plume area. The test setup allowed the collection of a large portion of the exhaust plume, and perchlorate was detected in most of the samples collected, due to the use of a very sensitive analytical method. The tests were conducted on four days and sampling was achieved after the static burning of, respectively, 2, 3, 4, and 6 Mk58 motors. The results obtained were consistent and reproducible, and it was estimated that only 2 mg of perchlorate was expelled as particulate matter for each Mk58 motor. Considering their flight range, it is concluded that the use of these rocket motors in live-fire training does not contribute significantly to the accumulation of perchlorate in the environment.

## Executive Summary

Live-fire training is an essential activity to maintain the readiness of our troops. R&D has been dedicated in the past years to the characterization of various types of training ranges and to the accumulation of munitions-related residues in the environment. Many training ranges have been visited and protocols have been drafted to efficiently characterize them. What was found in these ranges resulted from the accumulation of a wide variety of different live-firing activities. The munitions-related residues that have been studied extensively up to now are explosives, gun propellants, anti-tank rocket propellants, and heavy metals. They represent most of the compounds used in conventional weapons. Target areas are mostly impacted by explosives, while firing areas are impacted by unburned gun propellant residues. We need to better assess the specific impacts of the different activities that represent live-fire training. Perchlorate-based energetic materials have not been scrutinized yet for their potential accumulation in the environment, and this needs to be addressed. Perchlorate is an oxidizer widely used in solid rocket propulsion, and recently it has been detected in various groundwater reservoirs in the United States. In Canada, Environment Canada is putting together a database specifically on the levels of perchlorate in Canadian groundwater, and we have detected it in a few groundwater wells at a few training areas. It is a newly identified and important contaminant of concern, due to its potentially adverse human health impacts and its very low threshold criteria. Therefore, it was imperative to verify whether the live-fire training with AP-based rockets could lead to the accumulation of perchlorate in the environment. The goal of the present study was to conduct static firing of 15 Mk58 rocket motors and to measure the amount of perchlorate that was deposited. This rocket motor is used on the AIM-7 missile, which is widely used by both Canada and the United States as a medium range air-to-air weapon on their respective fighter jets. The study was conducted in collaboration between Canada and the United States and was held in June 2006 at the DRDC Valcartier test site. A test setup was designed to collect potential perchlorate particles ejected during static firing on a bench to concentrate the motor plumes in the smallest possible area. It was demonstrated that during normal burning conditions, perchlorate-based solid propellant motors generate very small quantities of perchlorate particles in the environment. If we consider the normal range of these rockets, reported to be on the order of 50 km, and the levels of perchlorate generated, the environmental impact of live-fire training with perchlorate-based motors is negligible in terms of the dispersion of particles. This report describes all the approaches taken to collect the samples and the results obtained from these experiments.

## Acknowledgments

The Director General of Aerospace and Engineering Program Management (DGAEPM) is greatly acknowledged for the provision of fifteen Mk58 rocket motors to allow the present study. Many thanks are addressed to the following personnel of the Propulsion group for their contribution to the safe handling and static ignition of the 15 rocket motors: Mrs. Michel Côté, Jean-Guy Hervieux, Marc Légare, and Christian Watters. Mrs. Michel St-Onge, Pierre Gosselin, and Michel Noel from Numerica and Adjum Degready, Adj Desbiens, Mr. Guy Barette and Mr. François Paquet of the Munitions Experimental Testing Center (METC) also are greatly acknowledged for their valuable support during the trial. Thanks to the Garrison Valcartier firefighters for their participation in the test setup. Thanks to Ms Susan Brown from Environment Canada for performing the analysis of our samples. Finally, the United States Strategic Environmental R&D Program (SERDP) is acknowledged for its financial support through SERDP project ER-1481. This chapter was reviewed by Dr. C.L. Grant, Professor Emeritus, Chemistry Department, University of New Hampshire, and by Dr. Thomas F. Jenkins, ERDC-CRREL.

## Introduction

Modern solid composite rocket propellants are based mostly on an ammonium perchlorate (AP) oxidizer dispersed in either hydroxyl- or carboxy-terminated polybutadiene (HTPB or CTPB). AP is a very good oxidizer that leads to high-performance, high-burning-rate rocket motors; as such, it has been used extensively in the past in many solid rocket propellant formulations, including its use by NASA Space Shuttle (Ref. 1). Perchlorates also are used in a number of other applications, including as a component of fireworks, pyrotechnics, flares, and explosives. Other uses include pharmaceuticals for hyperthyroidism, gas generators, electrolytes for lithium cells, and as chemical reagents. The occurrence of perchlorate in the environment is principally anthropogenic in nature. There are major drawbacks to the use of AP as an oxidizer in rocket propellants. Its combustion generates hydrochloric acid, which is a highly corrosive and non-environmental by-product that can generate acid rain and toxicity, and can decrease the air quality (Ref. 2).

This gaseous acidic emission is also easy to track because it may lead to visible white secondary smoke in the missile plume. Efforts have been dedicated in recent years to replace AP by other oxidizers, such as ammonium nitrate (Ref. 3, 4) that would avoid the production of hydrochloric acid. Unfortunately, the burning rates of ammonium-nitrate-based propellants were insufficient and, despite large efforts several years ago, did not lead to acceptable rocket

propellant formulations. More recently, ammonium dinitramide [ADN, NH<sub>4</sub>N(NO<sub>2</sub>)<sub>2</sub>], was introduced as an oxidizer in order to produce a new generation of environmentally friendly rocket propellants and for spacecraft propulsion (Ref. 5, 6). SERDP sponsors research in the area of the synthesis, evaluation, and formulation of oxidizers as alternatives to AP in missile propulsion applications (Ref. 7a).

Another strong drawback of the use of AP as an oxidizer in rockets is its potential dispersion in the environment upon its production, use, or demilitarization at the end of the rocket service life. Perchlorate salts are water-soluble and not significantly adsorbed by soil minerals or humic substances and hence are highly mobile in the environment. This chemical represents a health concern because, when ingested, it can disrupt the thyroid function by competitively inhibiting iodide transport (Ref. 8). Because of its potential adverse health effect, the U.S. Environmental Protection Agency (EPA) included perchlorate on its Drinking Water Candidate List 2 (Ref. 9). Health and ecological risks associated with perchlorate exposure are under investigation and SERDP is sponsoring projects to study the ecological risks of AP (Ref. 7b). Studies also are being conducted on potential treatments to remediate perchlorate in the environment (Ref. 10, 11). Debate on the acceptable levels of perchlorate in drinking water led to the adoption of a more stringent threshold criterion for perchlorate in drinking water. The discovery of widespread low levels of perchlorate in various aquifers in the United States (Ref. 10) has engaged the governmental regulatory agencies in an intensive analysis regarding perchlorate toxicology and the recommended daily dose exposure for humans (Ref. 12, 13). A reference dose of 0.0007 mg/kg/day of perchlorate was adopted by the US EPA in February 2005; this translates into a drinking water equivalent level of 24.5 µg/kg (Ref. 14).

These findings in turn dictate that the sources of this contaminant in the environment must be better defined in order to minimize its further dispersion. There are very few papers in the literature on the dispersion of perchlorate particles from the burning of AP-based rocket motors. Only one study was published, on the development of a method to predict potential perchlorate releases from accidental launch failures (Ref. 15). However, previous studies conducted on the dispersion of gunpowder residues in the environment following the firing of artillery and mortar rounds demonstrated that measurable amounts of gun propellant residues can be found near the gun exit (Ref. 16, 17).

The goal of this trial was to determine whether the firing of rocket motors in their normal firing conditions can lead to the dispersion and accumulation of unburned AP in the environment. To achieve this, the Canadian inventory was reviewed to identify a representative AP-based rocket motor that also is used by

the American military. AIM-7 missile rocket motors were identified as such, and a request was made to the Director General of Aerospace and Engineering Program Management (DGAEPM) to acquire 15 motors to conduct representative static burn tests. This request was accepted, and the 15 motors were shipped to Defence Research and Development Canada (DRDC) Valcartier from Cold Lake Air Force Base.

The AIM-7 Sparrow missile is a radar-guided air-to-air missile with a high explosive warhead (Fig. 6-1). It is widely used by Canadian, American, and North Atlantic Treaty Organization (NATO) forces and has been the main supersonic medium-range air-to-air missile of U.S. and Canadian fighter jets for many years (Ref. 18). It is propelled by an AP/CTPB solid propellant dual thrust rocket motor (Ref. 19). The Canadian version of the AIM-7 rocket is propelled by Mk58 Mod 5 motors.



Figure 6-1. Aim-7 rocket fired from an F18 fighter jet.

Prior to the static firing of the AP-based Mk58 motors, our setup was tested with Air Defence Anti-Tank System (ADATS) motors firing for tests that were conducted by the Propulsion Group to study low temperature operation (Ref. 20).

This chapter describes the static firing of the Mk58 Mod 5 rocket motors on a test bench at the DRDC Valcartier test area and the measurement of the AP residues expelled during combustion. Static firings of the rocket motors were conducted between June 21st and June 29th, 2006, and were co-sponsored by SERDP, DGAEPM, and the Sustain trust 12 SG.

## **Experimental Methods**

### *Field Work*

The trial was conducted at DRDC Valcartier Test Range, located within the Garrison Valcartier. ADATS motor firing was held between June 14th and 16th 2006, while MK58 tests were conducted between June 20th and June 28th. The ADATS trial was conducted by the Propulsion Group to test the low temperature ( $-40^{\circ}\text{C}$ ) operation of six ADATS rocket motors from various production lots. We used these firings to validate and prove our field setup, in preparation for the Mk58 trial. If feasible, sampling of the RDX-based ADATS residues would have been conducted, but it was not achieved because of various technical problems encountered. The Mk58 trial was conducted in four days, on June 20th, 22nd, 27th, and 28th where two, three, four, and six motors were fired, respectively. The meteorological conditions prevailing on these days were difficult and are reported in Table 6-1. Firing was not conducted on June 21st because of heavy rain conditions.

### *Material*

Six ADATS motors (Fig. 6-2) were statically fired after a conditioning period of 48 hours at  $-40^{\circ}\text{C}$ . Fifteen Mk58 Mod 5 (Lot QZC) rocket motors (P/N 1131AS200-1, NSN 1337-01-150-7939) were obtained from the Director General Aerospace Engineering Program Management (Fig. 6-3). They were allocated to DRDC Valcartier's environmental study and sent from Cold Lake depot approximately one month prior to the trial. Aluminium witness plates, 1 m  $\times$  1 m  $\times$  3 mm, were placed in front of the rocket nozzle to collect potential residues (Fig. 6-4). They were wiped with cotton gauze, using distilled water to wet them when dry meteorological conditions prevailed. Water traps also were used in the second setup to catch and trap perchlorate particles. Commercially available rectangular aluminum pans (39.2  $\times$  32.3  $\times$  7.9 cm) were buried in the soil at a depth until flush with the surface and filled with distilled water (300–500 mL).

Rocks were placed in the pans to stabilize them and prevent their movement by the rocket motor plume (Fig. 6-5). The water in the traps was collected using 1-L amber glass containers and the exact volumes were measured. On rainy days, the rain water accumulated in the traps and the total volume of water was collected. On June 20th, 16 traps were used; 20 traps per day were used afterward.



**Figure 6-2. ADATS motor.**



**Figure 6-3. Mk58 motor.**



**Figure 6-4. Aluminum witness plate.**



**Figure 6-5. Water trap.**

### *Propellant Composition*

#### **ADATS Motors**

ADATS motors use cross-linked propellant mixed with RDX crystals. They contain 19.6 kg of cross-linked double-base propellants, with 7.8% by weight of binder, 62% of RDX, 25.88% of plasticizers, and a few percent of thermal stabilizers, ballistic modifiers, and acoustic additives (Ref. 20).

#### **Mk58 Motors**

The AIM-7 Mk58 rocket motor is 203 mm in diameter by 1514 mm long. The case is constructed from steel, has a wall thickness of 1.880 mm, and contains 61 kg of CTPB-based propellant. It uses a dual-grain propulsion system with two types of propellants to provide a boost-sustain thrust profile. Both propellants are based on AP dispersed in a CTPB matrix, but their formulations are slightly different in terms of relative percentage of ingredients. The ratio of sustain-to-boost propellant is 70 to 30 percent by volume (Ref. 21). Other ingredients include plasticizers and phenyl-beta-naphthylamine (PBNA) as an anti-oxidant. This latter compound is present at less than 1% by weight in the propellant but it might be considered as a health hazard since it has adverse toxicological impacts. It was not included as an analyte in the present study, but depending on the levels of residues deposited, it could be important in further studies. The detailed formulations of these propellants are considered proprietary information. However, the fact that Mk58 motors contain 47 kg of AP can be disclosed.

### *Field Setup and Sampling Strategy*

The initial setup was tested by firing the six ADATS motors before firing the Mk58 motors. This first setup was based on a preliminary study conducted in 2004 that evaluated the gaseous emissions from the static firing of ADATS motors (Ref. 22). The deposition area was secured by using concrete blocks in a “U shape” (eleven 2-ft × 2-ft × 6-ft blocks), installed 8 m away from the motor nozzle (Fig. 6-6). These concrete blocks were intended to protect the witness plates against the blast from the motors and to reduce the disturbances at the surface of the soil. A concrete pad 17 m wide by 12 m long was located directly in front of the test stand and five aluminum witness plates were screwed to its surface, 10 m behind the motor nozzle and 1.5 m from each other. Three polyethylene tarps were used as soil cover to minimize the potential cross contamination from the underlying soil and were installed from the concrete pad to 35 m from the nozzle. Twenty witness plates were equally spaced and placed on the three tarps at, respectively, 13, 16, 19, 22, and 25 m from the nozzle (Fig.

6-7). Sandbags were deposited on the leading edge of the aluminum witness plates to stabilize them during the firing of the rockets (Fig. 6-8). The tarps also were tied up with sandbags. Prior to both ADATS and Mk58 static firing, the fire department of Garrison Valcartier was tasked to wash the entire concrete surface and concrete block to minimize potential cross contamination from past trials (Fig. 6-9). They washed the surface on June 14th and June 20th.



**Figure 6-6. Installation of the concrete wall.**

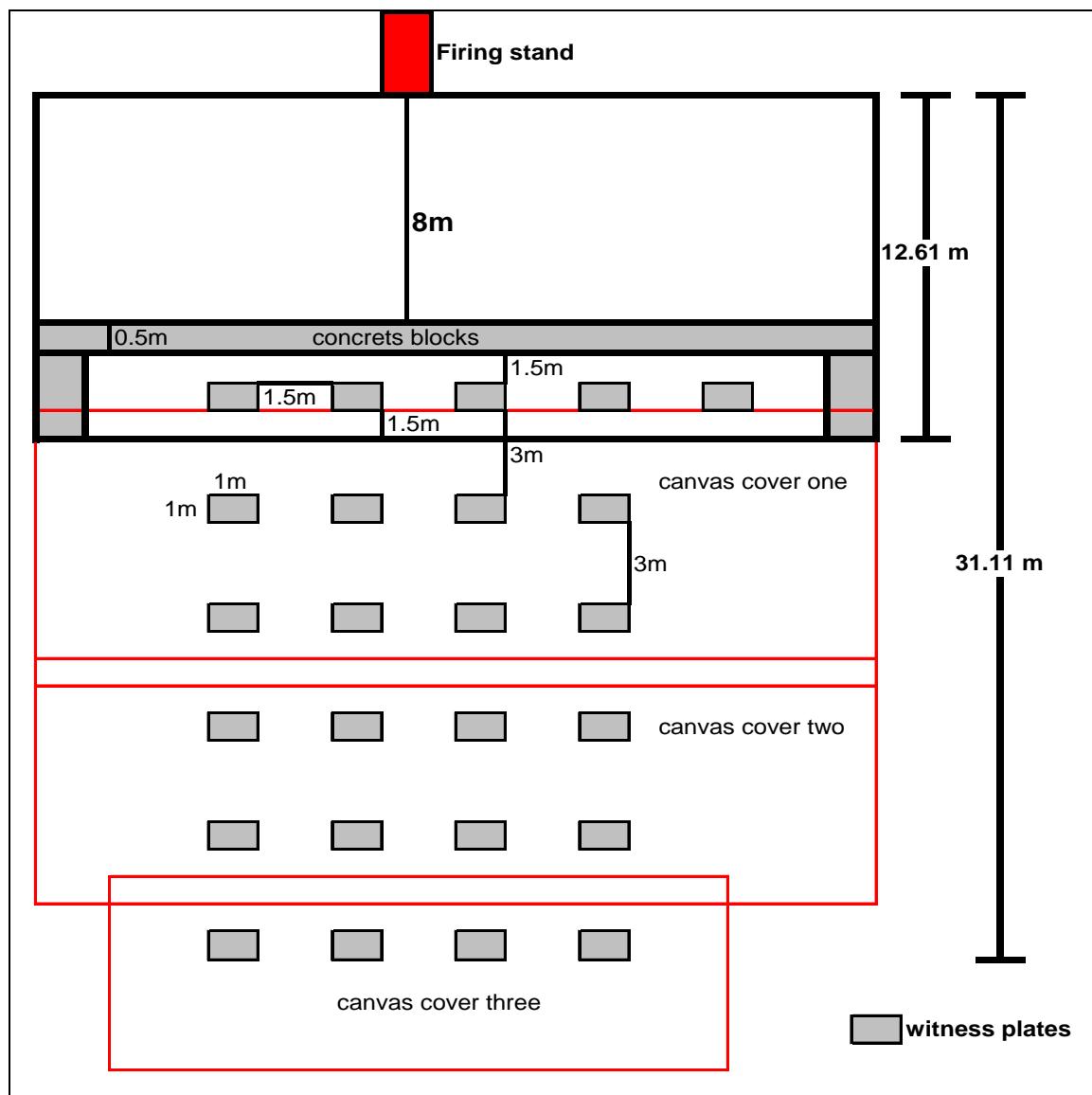


Figure 6-7. Initial setup diagram.



**Figure 6-8. Initial test layout.**



**Figure 6-9. Washing the concrete surfaces.**



**Figure 6-10. Initial layout after ADATS static firings.**

The initial setup failed in allowing the collection of residues from the static firings. Furthermore, as a result of the heat developed by the rocket blast, seven sandbags and the first tarp melted (Fig. 6-10). Moreover, visual observation of the firings proved that our plates were not correctly located, since the plume deposition area was much larger than expected (Fig. 6-11). The ADATS rocket blast was obviously more powerful than expected, and a realistic idea of how far and fast the blast of an Mk58 motor would carry was required. A simulation of plume velocity versus distance was carried out to show that, at a distance of 200 meters, the speed of the blast would still be 10 m/s. Consequently, no residues were sampled from the ADATS firings because the plates were too close and the tarp melted on many of them. The use of witness plates as the receptacle for particulate material in such a highly turbulent environment was also questioned.



**Figure 6-11. ADATS static firing.**

Keeping this information in mind, it was decided to extend the sampling template up to 200 meters from the firing stand and to remove the polyethylene tarps. Witness plates were placed in a triangular pattern using a wider sampling area. The plates were installed at 10, 50, 100, and 150 m from the motor nozzle (P0, P1, P2, and P3 rows). Water traps were also used as receptacles for perchlorate particles and spread out evenly in the plume deposition area (W1 to 20). These traps were used to minimize the potential of losing the particles due either to rain conditions, wind, or turbulence. The second field setup, illustrated in Figure 6-12, was used on June 20th and included 16 water traps. A third and final setup then was used until the end of the trial by adding an additional four water traps (Fig. 6-13, 6-14). Our setup was correctly positioned based on the visual observation of the plumes generated by the Mk58 firings (Fig. 6-15).

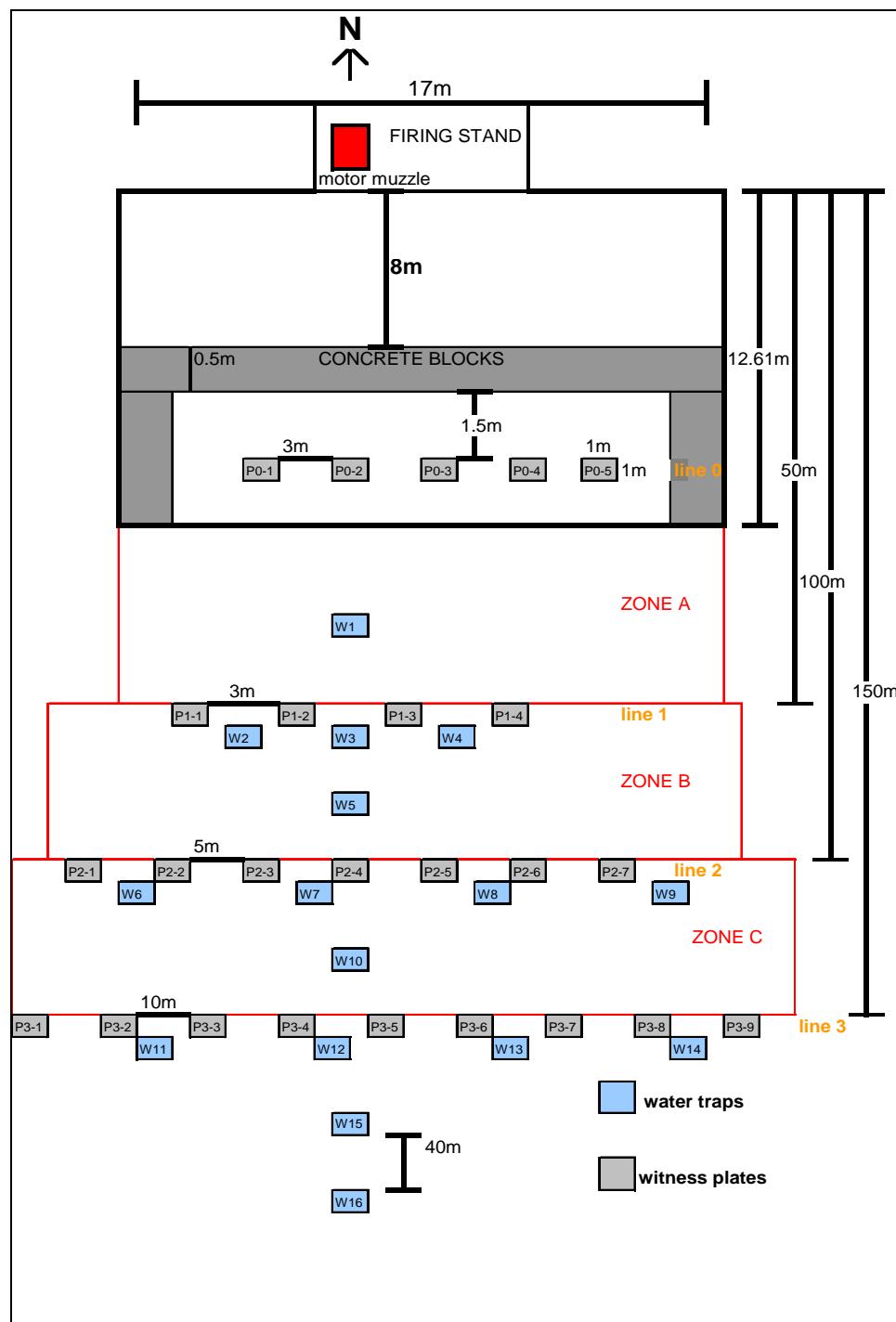


Figure 6-12. Second setup diagram.

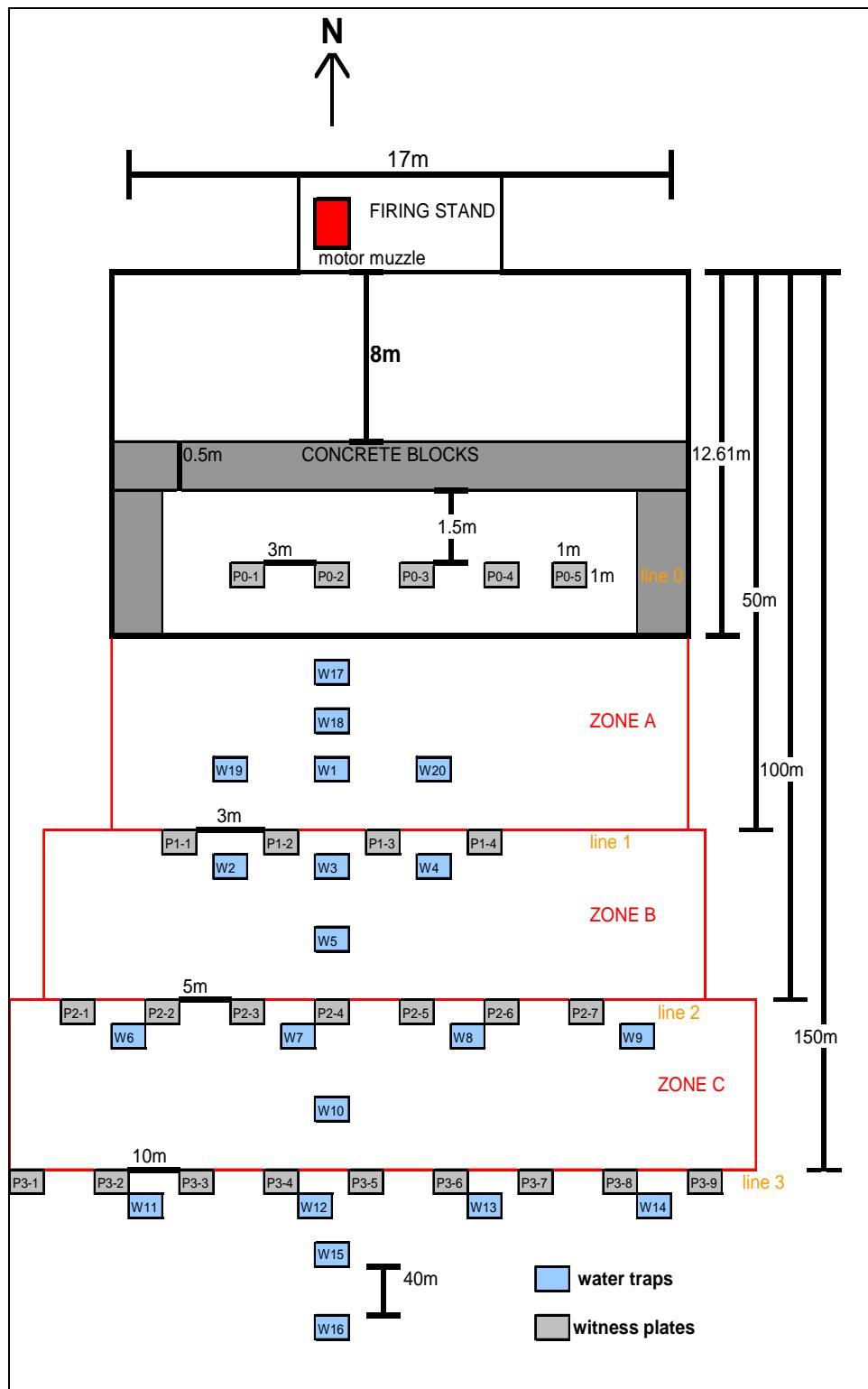


Figure 6-13. Third setup diagram.



Figure 6-14. Third setup.



Figure 6-15. Mk58 static firing.

Wipes from witness plates in the same rows were combined, based on the small area covered by each plate ( $1\text{ m}^2$ ). They were designated as P0 to P4-ALL-AIM06-trial. As such, the area sampled per row represented a total area of 5, 4, 7, and  $9\text{ m}^2$ , respectively, for rows labelled P0, P1, P2, and P3. Water trap samples were labelled W-1 to 20-AIM06- trial #. The area covered by one water trap was  $0.127\text{ m}^2$ .

On a daily basis, the following was accomplished:

**Day one, June 20th, Test 1.**

Two motors were fired at 14h00 and 14h20. The firings were done under light rain and then heavy rain prevailed. Witness plates were not sampled because of heavy rain and flooding of the plates. The 16 water traps were sampled after the two motors were fired. The labelling was W 1 to 16, AIM06-1.

**Day two, June 22nd, Tests 2, 3, and 4.**

Three motors were fired at 9h20, 9h55, and 10h35 under light rain conditions. Witness plates were sampled after each firing. The labelling was P0 to P3-AIM06-ALL-2 to 4. Nineteen water traps were sampled (Trap 20 was blown away by the blast) after the three firings and were labelled W 1 to 19-AIM06-2.

**Day three, June 27th, Tests 5 and 6.**

Four motors were fired at 10h00, 10h50, 11h17, and 11h45 under light rain conditions. Witness plates were sampled after the first firing (Test 5) and then after the three remaining motors (Test 6). They were labelled P0 to P3-AIM06-5 and 6. Twenty water traps were sampled after the four motors and were labelled W 1 to 20-AIM06-3.

**Day 4, June 28th, Tests 7, 8, 9, and 10.**

Six motors were fired under cloudy conditions at 8h46, 9h22, 9h50, 10h16, 10h51, and 11h20. Witness plates were sampled after the first motor (Test 7), the second motor (Test 8), the third and fourth motors (Test 9), and the fifth and sixth motors (Test 10). They were labelled P0 to P3-AIM06-7, 8, 9, and 10. Twenty water traps were sampled after the six motors and were labelled W 1 to 20-AIM06-4.

**Test Stand**

A mobile test stand, designed to be installed rapidly in an open-air experimental site, was used during the firing of six ADATS and fifteen AIM-7 (Fig. 6-16, 6-17). This installation was designed and built by DRDC scientists to study the plume of different types of rocket motors. A special mounting system was

fabricated to safely retain the Mk58 motors during firing (Fig. 6-18). This installation allows the user to measure various characteristics of rocket motors such as thrust, chamber pressure, and plume signature. The hardware to support and hold the motor was designed to characterize its signature without excessive masking in any 360° rotational direction. This test stand is vertically adjustable from 1.0 to 3.3 meters from the ground. The assembly can revolve, varying the firing axis in any horizontal direction, by pivoting the inner stand of the base. It is also composed of an angular section, which, once adjusted to the test stand, allows the user to vary the firing angle in a vertical sense. This test stand, which is equipped with lateral stabilizers and cable stabilizers, may be used to test rocket motors that produce up to 90 kN of thrust.



**Figure 6-16. Motor static test stand.**

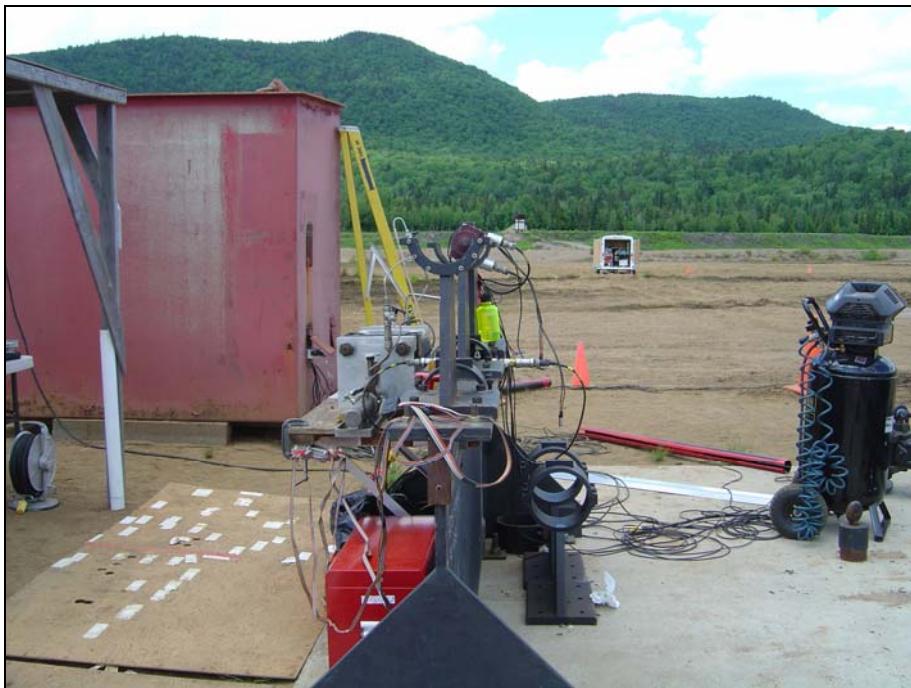


Figure 6-17. Front view of the static test stand.



Figure 6-18. Mk58 motor holder.

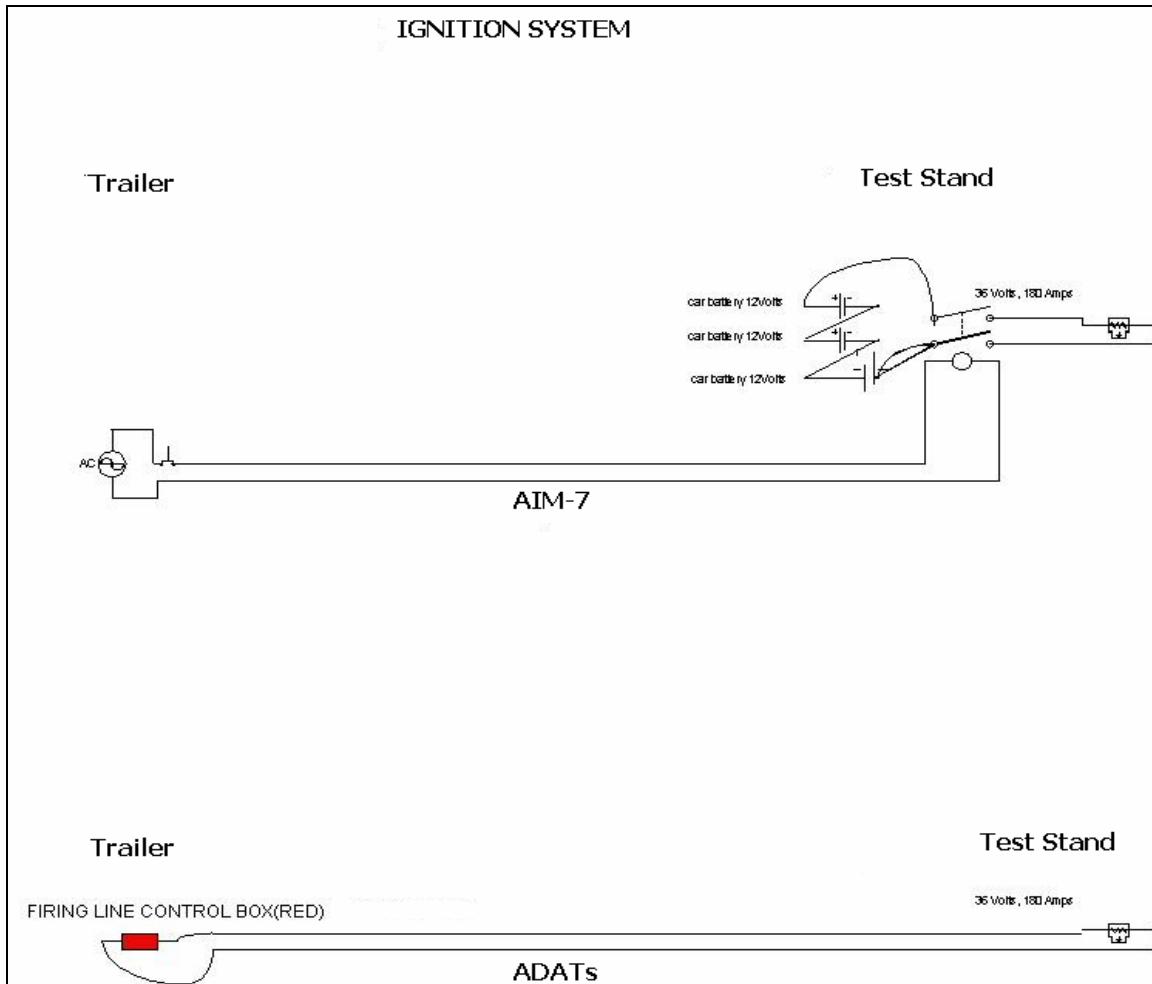
For ADATS and Mk58 firings, the motors were positioned horizontally at 1.5 m off the ground. Unobstructed views of the motor were possible from at least 200 m in any direction and allowed various monitoring and high speed recording of the firing events (Fig. 6-19).



**Figure 6-19. Test bench at a distance.**

#### *Motor Ignition*

All motors were ignited remotely and supervised by an experienced ammunition technician. All personnel were either in special shelters or at the trailer, located approximately 300 m from the test bench. The ignition system consists of three batteries mounted in parallel placed at the base stand and connected to a 120-volt power supply. When the power supply was connected to the AC system and engaged by the ammunition technician situated in the trailer, the loop closed and ignited the squib of the rocket (Fig. 6-20). A five-minute period had to be respected for safety after each motor firing prior to inspection by the ammunition technician, who then gave the authorization to come back to the test site for sampling. A delay of 5 to 10 minutes resulted between firing and sampling.



**Figure 6-20. Ignition systems.**

#### *High-Speed Camera*

All motor firings were recorded using a monochrome high-speed camera from Canadian Photonics Labs. It has a maximum resolution of  $504 \times 504$  pixels with a camera buffer memory of 8.6 gigabytes and a maximum frame rate speed of 91,250 frames per second (fps) (resolution of  $504 \times 24$ ). The camera's data acquisition and control system software was supplied with portable PC hardware. The communication between the portable PC hardware and the camera was achieved with 100-gigabit Ethernet connectivity. An external trigger source was used to manually trigger the camera during the event. The camera was located 70 m away, to the side and slightly behind the thrust stand, at 120 degrees for the ADATS and at 90 degrees for the Mk58. The main focus of the use of this camera by the Propulsion Group was to evaluate failure, if any, at the blast tube

area of the rocket motor in the ADATS firings. The team also recorded the Mk58 firings to see any evidence of perchlorate particle ejection. The camera was set to operate at 1000 fps at maximum resolution. However, due to the greater focal length of the lens and consequently less light being available, the shutter speed and gain were increased to 700 and 600  $\mu$ s, respectively. The aperture was set at F8.0 for maximum opening of the lens. The recording time of each event was set between 5 and 7 seconds for ADATS and approximately 20 seconds for the Mk58 by manual trigger. The field of view for the Mk58 was cropped to 504  $\times$  120 pixels, which allowed a more manageable camera memory buffer for the 20-second recording.

#### *Sample Extraction and Analysis*

Water collected in water traps was brought to DRDC Valcartier laboratory at the end of each day. Samples were immediately filtered using disposable 60-mL plastic syringes and a 0.45- $\mu$ m syringe filter, and their exact volumes were measured and are reported in Table 6-2. An aliquot of 20 mL was poured into 50-mL high-density polyethylene containers. Samples were stored with a large headspace to avoid anaerobic degradation, kept at 4°C, and sent within 48 hours by express transport to Environment Canada for analysis. One field blank was included by processing a water sample in the exact same way as for the test samples, and a laboratory blank was included by processing distilled water in the laboratory with the same procedure used for the water trap samples. They were labelled, respectively, P-5-AIM06-B2 and P-5-AIM06-B1.

The witness plate wipes were brought to the laboratory at the end of each day. All samples were wet due to the rainy conditions prevailing on the first three days of trial. A volume of 100 mL of distilled water was added to the jars, which were vigorously agitated manually three to five times and then sonicated for 30 minutes. The water extracts and the wipes were filtered by putting the soaked wipes into 250-mL plastic syringes using 0.45- $\mu$ m syringe filters. The wipes were further rinsed by adding 50 mL of distilled water to collect any residual perchlorate. The total water volumes extracted were noted and are reported in Table 6-3. An aliquot of 20 mL was poured into a 50-mL high-density polyethylene container. Samples were stored with a large headspace to avoid anaerobic degradation, kept at 4°C, and sent within 48 hours by express carriage to Environment Canada for analysis.

The analysis was conducted by Environment Canada using ion chromatography coupled to a tandem mass spectrometer. Separation was performed using a Dionex 2500 system equipped with an autosampler, a GP50 pump, an EG50 eluant generator, and ED50 conductivity detector on a Dionex IONPAC AS20

analytical column ( $2 \times 250$  mm) with a Dionex IONPAC AG20 guard column ( $2 \times 50$  mm). Using an EG50 eluant generator, a 35-mM potassium hydroxide solution isocratic eluant was run at a flow rate of 0.35 mL/min. An Agilent 1100 pump was used to tee in 90/10 (acetonitrile/water) at 0.2 mL/min at the mass spectrometer source. Total flow into the mass spectrometer was 0.55 mL/min. Injection volume was 100  $\mu$ L. Under these conditions, the retention time of perchlorate was  $\sim$ 13.5 min. An API 2000 (MDS Sciex, Ontario, Canada) triple quadrupole tandem mass spectrometer, operated in the electrospray ionization mode, was used for the detection of perchlorate using Analyst version 1.4 software. The instrument was run in the negative ion mode, and each quadrupole was set to unit mass resolution. Three multiple reaction monitoring transitions were monitored: m/z 99-83, m/z 101-85 (for native perchlorate), and m/z 107-89 (for enriched perchlorate). Quantitation was accomplished using an internal standard method ( $\text{C118O}_4^-$ ) at 1  $\mu\text{g}/\text{L}$ . Instrument calibration was performed by analyzing standards at 0.05, 0.1, 0.2, 0.5, 1, 5, 10, 20, and 40  $\mu\text{g}/\text{L}$  in reagent water. To demonstrate that the instrument was properly calibrated throughout the analysis, a continuing calibration verification standard was analyzed every 10 samples. The minimum detection limit achieved was 0.011  $\mu\text{g}/\text{L}$ , while the practical quantitation limit was 0.05  $\mu\text{g}/\text{L}$ .

## Results and discussion

### *Test Setup and Sampling Strategy*

The collection of perchlorate particles from the static burning of large rocket motors was not an easy task. The first setup used for the ADATS motors proved to be inefficient because it used a plastic tarp that melted. Moreover, it was clear that our sampling area was not large enough and that most of the plume fell outside of the boundary of our setting. The use of witness plates when compared to the use of water traps showed many weaknesses. In heavy rain or wind conditions, witness plates cannot be used because particles are either washed or blown away. In light rain and soft wind conditions, such as the ones that prevailed the first three days of sampling, the use of witness plates was still acceptable. Their use also involves an extraction step, when wipes are extracted by distilled water. In comparison, the use of water traps greatly reduces the risk of analyte loss, so no extraction step is needed. Soil samples also were collected before the test in four large areas within our sampling template, and we planned to sample the same areas at the end of each day. For the first three days, this was not done because in rainy conditions there was no confidence in the results obtained because perchlorate is a highly soluble and labile analyte. On the fourth day, soil samples were collected, but unfortunately the results were not available at the

time of this report's production. However, soil extractions may lead to potential interference from other compounds, loss of analyte in the extraction step, and cross-contamination from past activity on the test site, so water traps are still considered the best sampling approach.

The global area considered in the final setup is 4000 m<sup>2</sup>, with dimensions 20 m by 200 m. It was not possible to expand our sampling template area because we reached the limit of the open area with the presence of a concrete wall at one end, and a dense vegetated area at a distance of 220 m from the motor nozzle.

### *Meteorological Conditions*

The meteorological conditions pertaining while the trial was conducted are presented in Table 6-1. Days 1, 2, and 3 were rainy, while the fourth day was cloudy without rain. The wind direction and speed are reported, and it has to be pointed out that the highest speed (5 knots) still represents a light wind. It was evident that the use of witness plates was less useful than the water traps for this application, but it was decided to pursue both methods to compare them. On Day 1, after the firing of the second motor, heavy rain and lightning prevented the collection of samples from the witness plates. Only the water traps were collected. The final volume of each trap was increased due to the large contribution of the heavy rainfall. The light rain conditions prevailing the first three days of testing had the advantage of avoiding dust cross contamination from the soil, and helped in wetting the witness plates to improve the adhesion of AP particles.

We have carefully examined the results in relationship with the wind directions and speed, and no tendency could be established between deposition patterns and wind conditions. As stated earlier, the wind speeds prevailing in the four days of trial were light, and their influence can be considered negligible when compared to velocities in most of the rocket plume.

### *Water Trap Results*

The concentration measured in water samples collected in the traps, the total volume of water collected, the mass per trap, per square meter, and per motor are presented in Tables 6-2 to 6-4. Table 6-2 presents the results for Days 1 and 2, while Tables 6-3 and 6-4 present the results for Days 3 and 4, respectively. The surface area covered by the water in one trap was 0.127 m<sup>2</sup>. Some concentration estimates lie between the minimum detection and practical quantitation limits of the method, so we can conclude that our test setup allowed the detection of perchlorate, with, in some cases, a lower level of confidence because results are at the limits of the analytical method. If such a high sensitivity method were

not used, non-detectable concentrations of perchlorate would have been obtained for most of the samples. Field and trip blanks were included for water traps and the results came back non-detected, which improved the confidence in our samples.

**Table 6-1. Meteorological conditions.**

Date	Time	Meteorological condition	Wind speed (Knots)	Wind direction	Temperature (° C)
20 June	14h00	light rain	4	NE	20.8
20 June	14h20	light/heavy rain	4	NE	20.8
22 June	09h20	light/heavy rain	4	S	16
22 June	09h55	rain	3	SO	16
22 June	10h35	rain	3	S	16
28 June	10h00	light rain	2	SO	17.5
28 June	10h50	light rain	1	SO	17.5
28 June	11h17	light rain	2	SO	18
28 June	11h45	light rain	2	SO	18.3
29 June	8h46	clouds/no rain	4 to 5	N	21
29 June	9h22	clouds/no rain	5 to 8	NO	21
29 June	9h50	clouds/no rain	5 to 8	NO	21
29 June	10h16	clouds/no rain	5 to 8	NO	21
29 June	10h51	clouds/no rain	5 to 8	NO	21
29 June	11h20	clouds/no rain	5 to 8	NO	21

On Day 1 (Table 6-2), measured concentrations were quite homogenous, with the exception of Trap 15, located 172 m from the motor nozzle. In general, perchlorate was detected in an average concentration of  $0.5 \mu\text{g}/\text{m}^2$  per motor. No comparison for Day 1 between traps and plates can be established because the plates were not sampled. Results for Day 2 were quite similar, with even less variation between samples. On Days 3 and 4, we observed a few samples that present higher concentrations of perchlorate particle dispersed in the vicinity of the motor nozzle. On Day 3 (Table 6-3), samples labelled W-17, 18, 19, and 20 present concentrations one or two orders of magnitude higher than other samples and appear in red type in the table. It was decided to calculate the average concentration dispersed in two separate areas, the first one being nearest to the

nozzle with a dimension of 20 m × 50 m (1000 m<sup>2</sup>), and the second one in the furthest 20 m × 150 m (3000 m<sup>2</sup>). On Day 4, samples W-1 and W-20, located respectively at 12 and 62 m from the motor nozzle, present higher concentrations of perchlorate, while other samples show slightly lower levels than the first three days, with an average concentration of 0.2 µg/m<sup>2</sup> per motor.

**Table 6-2. Water trap results, 20 and 21 June.**

Sample	Perchlorate (µg/L)	Volume (L)	µg/trap	µg/m <sup>2</sup>	µg/m <sup>2</sup> per motor
<b>Day 1, two motors, heavy rain</b>					
W-1-AIM06-1	0.05	1.94	0.10	0.77	0.38
W-2-AIM06-1	0.04	1.81	0.07	0.57	0.29
W-3-AIM06-1	0.09	1.99	0.18	1.41	0.71
W-4-AIM06-1	0.04	2.83	0.11	0.89	0.45
W-5-AIM06-1	0.07	2.40	0.17	1.33	0.66
W-6-AIM06-1	0.11	2.03	0.22	1.77	0.88
W-7-AIM06-1	0.03	2.47	0.07	0.59	0.29
W-8-AIM06-1	0.03	1.95	0.06	0.46	0.23
W-9-AIM06-1	0.18	1.26	0.23	1.79	0.90
W-10-AIM06-1	0.07	1.74	0.12	0.96	0.48
W-11-AIM06-1	0.07	2.00	0.14	1.10	0.55
W-12-AIM06-1	0.05	1.86	0.09	0.73	0.37
W-13-AIM06-1	0.05	1.76	0.09	0.69	0.35
W-14-AIM06-1	0.03	1.76	0.05	0.42	0.21
W-15-AIM06-1	0.21	2.16	0.45	3.59	1.79
W-16-AIM06-1	0.03	0.95	0.03	0.23	0.11
Average					0.5
Standard deviation					0.4

**Table 6-2 (cont'd). Water trap results, 20 and 21 June.**

Sample	Perchlorate ( $\mu\text{g}/\text{L}$ )	Volume (L)	$\mu\text{g}/\text{trap}$	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$ per motor
<b>Day 2, three motors, light rain</b>					
W-1-AIM06-2	0.35	0.70	0.24	1.92	0.64
W-2-AIM06-2	0.49	0.37	0.18	1.43	0.48
W-3-AIM06-2	0.33	0.56	0.18	1.46	0.49
W-4-AIM06-2	0.81	0.68	0.55	4.33	1.44
W-5-AIM06-2	0.19	0.60	0.11	0.89	0.30
W-6-AIM06-2	0.42	0.41	0.17	1.36	0.45
W-7-AIM06-2	0.12	0.68	0.08	0.65	0.22
W-8-AIM06-2	0.22	0.67	0.15	1.16	0.39
W-9-AIM06-2	0.23	0.63	0.15	1.15	0.38
W-10-AIM06-2	0.41	0.18	0.08	0.59	0.20
W-11-AIM06-2	0.15	0.57	0.09	0.68	0.23
W-12-AIM06-2	0.29	0.44	0.13	1.01	0.34
W-13-AIM06-2	0.14	0.37	0.05	0.41	0.14
W-14-AIM06-2	0.24	0.54	0.13	1.03	0.34
W-15-AIM06-2	0.18	0.58	0.10	0.82	0.27
W-16-AIM06-2	0.27	0.23	0.06	0.50	0.17
W-17-AIM06-2	0.50	0.54	0.27	2.12	0.71
W-18-AIM06-2	0.15	0.93	0.14	1.10	0.37
W-19-AIM06-2	0.23	0.85	0.19	1.54	0.51
Average					0.4
Standard deviation					0.3

On the last two days of the trial, the pH of the water traps was recorded with pH paper to verify the influence of the hydrochloric acid plume. Lower pH values were measured in the area located between 12 and 62 m from the motor nozzles (Tables 6-3 and 6-4). The hydrochloric acid produced by the efficient combustion of perchlorate is preferentially deposited in this area. Solid particles will travel farther than gaseous emissions in soft wind conditions, and that is

what we observed with detectable levels of perchlorate at 200 m from the motor nozzle. The dispersion area of solid perchlorate particles is wider than our sampling template because we do not reach the boundary zone, where no perchlorate was detected in our traps. This means that we underestimated the total amount of perchlorate dispersed. We observed a slight decrease of concentrations measured with distances, but the dispersion pattern was quite homogeneous, with comparable levels at almost all sampling locations.

#### *Witness Plate Results*

Results for the second day of the trial on June 22nd are presented in Table 6-5 and the results for the third and fourth days of the trial are presented in Table 6-6.

In Table 6-5, results were not available for three samples, due to problems encountered with the analytical method at Environment Canada. The concentrations detected in water samples extracted from the wipes, as well as the volume of water used for the extraction, are reported. This allowed the calculation of the quantity of perchlorate in  $\mu\text{g}$  dispersed per row, and by dividing by the number of plates in each row (row 0 = 5 plates, row 1 = 4, row 2 = 7, and row 3 = 9), the quantity dispersed per square meter could be determined since each witness plate had a surface of  $1 \text{ m}^2$ . This allowed the calculation of the quantity dispersed per square meter per motor and, for the second day, it can be seen that most of the area sampled presented similar concentration ranges. A slight decrease in concentration with distance can be seen, with the exception of the row located at a distance of 100 m for the third motor, where the concentrations measured were twice the one in other rows. This might be explained by a motor that would have had a poorer combustion and spread more particles in the vicinity of the nozzle or else by the meteorological conditions. The high-speed camera video allowed the visual observation of particle emissions, especially in the sustain portion of the motor. The average concentration per square meter was calculated and this result presents an acceptable standard deviation. This suggests that the static burning of three motors on Day 2 generated the deposition of  $0.2 \mu\text{g}/\text{m}^2$  of perchlorate particles in a global area of  $4000 \text{ m}^2$ .

**Table 6-3. Water trap results, 28 June.**

Sample	Perchlorate (µg/L)	Volume (L)	µg/trap	µg/m <sup>2</sup> per motor	µg/m <sup>2</sup> per motor	pH
Day 3, four motors, light rain						
W-1-AIM06-3	0.21	0.35	0.07	0.58	0.15	3
W-2-AIM06-3	0.22	0.40	0.09	0.69	0.17	4
W-3-AIM06-3	0.09	0.31	0.03	0.22	0.06	4
W-4-AIM06-3	0.12	0.30	0.04	0.28	0.07	3
W-5-AIM06-3	0.12	0.29	0.03	0.27	0.07	6
W-6-AIM06-3	0.28	0.38	0.11	0.83	0.21	6
W-7-AIM06-3	0.53	0.37	0.19	1.53	0.38	6
W-8-AIM06-3	0.28	0.36	0.10	0.79	0.20	6
W-9-AIM06-3	0.39	0.41	0.16	1.26	0.31	6
W-10-AIM06-3	0.19	0.37	0.07	0.56	0.14	6
W-11-AIM06-3	0.11	0.46	0.05	0.40	0.10	6
W-12-AIM06-3	0.07	0.36	0.03	0.20	0.05	6
W-13-AIM06-3	0.04	0.37	0.01	0.12	0.03	6
W-14-AIM06-3	0.11	0.32	0.04	0.28	0.07	6
W-15-AIM06-3	0.16	0.39	0.06	0.50	0.12	6
W-16-AIM06-3	0.36	0.33	0.12	0.95	0.24	6
Average (1 to 16)					0.20	
Standard deviation (1 to 16)					1.10	
W-17-AIM06-3	28.8	0.23	6.62	52.32	13.08	0
W-18-AIM06-3	5.89	0.33	1.94	15.35	3.84	2
W-19-AIM06-3	16.20	0.27	4.37	34.55	8.64	4
W-20-AIM06-3	5.70	0.30	1.72	13.6	3.40	3
Average (17 to 20)					7.24	
Standard deviation (17 to 20)					5.08	

**Table 6-4. Water trap results, 29 June.**

Sample	Perchlorate (µg/L)	Volume (L)	µg/trap	µg/m <sup>2</sup> per motor	µg/m <sup>2</sup> per motor	pH
Day 4, six motors, no rain						
W-1-AIM06-4	4.51	0.60	2.68	21.20	3.53	3
W-2-AIM06-4	0.10	0.87	0.09	0.68	0.11	4
W-3-AIM06-4	0.08	0.68	0.05	0.43	0.07	5
W-4-AIM06-4	0.20	0.56	0.11	0.88	0.15	5
W-5-AIM06-4	0.20	0.51	0.10	0.80	0.13	6
W-6-AIM06-4	0.34	0.43	0.15	1.15	0.19	6
W-7-AIM06-4	0.29	0.40	0.12	0.91	0.15	6
W-8-AIM06-4	0.12	0.50	0.06	0.47	0.08	6
W-9-AIM06-4	0.28	0.35	0.10	0.77	0.13	6
W-10-AIM06-4	0.09	0.55	0.05	0.39	0.06	6
W-11-AIM06-4	0.13	0.60	0.08	0.62	0.10	6
W-12-AIM06-4	0.05	0.49	0.02	0.19	0.03	6
W-13-AIM06-4	0.02	0.81	0.02	0.13	0.02	6
W-14-AIM06-4	0.14	0.61	0.09	0.67	0.11	6
W-15-AIM06-4	0.23	0.74	0.17	1.35	0.22	6
W-16-AIM06-4	0.09	0.67	0.06	0.48	0.08	6
W-17-AIM06-4	0.42	0.23	0.10	0.76	0.13	6
W-18-AIM06-4	0.74	0.82	0.61	4.81	0.80	4
W-19-AIM06-4	0.30	0.54	0.16	1.27	0.21	3
W-20-AIM06-4	2.09	0.61	1.27	10.04	1.67	3
Average (2 to 19)					0.16	
Standard deviation (2 to 19)					0.17	
W-21-AIM06-B	nd	field blank				
W-22-AIM06-B	nd	trip blank				

<b>Table 6-5. Witness plate results for 22 June.</b>					
<b>Sample</b>	<b>Perchlorate (<math>\mu\text{g/L}</math>)</b>	<b>Volume (L)</b>	<b><math>\mu\text{g}/\text{row}</math></b>	<b><math>\mu\text{g}/\text{m}^2</math></b>	<b><math>\mu\text{g}/\text{m}^2</math> per motor</b>
<b>Day 2, one motor</b>					
P0-ALL-AIM06-2	to be determined	0.13			
P1-ALL-AIM06-2	2.66	0.20	0.52	0.13	0.13
P2-ALL-AIM06-2	11.60	0.09	1.01	0.14	0.14
P3-ALL-AIM06-2	4.21	0.26	1.08	0.12	0.12
P0-ALL-AIM06-3	to be determined	0.10			
P1-ALL-AIM06-3	to be determined	0.05			
P2-ALL-AIM06-3	4.74	0.18	0.87	0.12	0.13
P3-ALL-AIM06-3	3.92	0.19	0.76	0.08	0.08
P0-ALL-AIM06-4	4.65	0.16	0.74	0.149	0.15
P1-ALL-AIM06-4	2.55	0.16	0.41	0.103	0.10
P2-ALL-AIM06-4	12.60	0.21	2.58	0.369	0.37
P3-ALL-AIM06-4	5.15	0.19	0.99	0.110	0.11
<b>Day 2, average per motor</b>					
Average					0.15
Standard deviation					0.09

Results for Day 3 presented in Table 6-6 are fairly homogeneous and showed no real trend with distance from the first motor nozzle. The second sampling after three motors showed higher concentrations for Rows 0 and 1. On Day 4, levels were relatively homogeneous and lower than for the other days; this could be attributed to the absence of light rain and the higher potential for particle loss. Results on Day 3 are not normally distributed for the four sets of samples with a standard deviation superior to the average concentration.

<b>Table 6-6. Witness plate results for 28 and 29 June.</b>					
<b>Sample</b>	<b>Perchlorate (<math>\mu\text{g}/\text{L}</math>)</b>	<b>Volume (L)</b>	<b><math>\mu\text{g}/\text{row}</math></b>	<b><math>\mu\text{g}/\text{m}^2</math></b>	<b><math>\mu\text{g}/\text{m}^2</math> per motor</b>
<b>Day 3, one motor</b>					
P0-ALL-AIM06-5	1.11	0.26	0.29	0.06	0.06
P1-ALL-AIM06-5	0.53	0.29	0.16	0.04	0.04
P2-ALL-AIM06-5	1.53	0.20	0.30	0.04	0.04
P3-ALL-AIM06-5	2.64	0.19	0.49	0.05	0.05
<b>Day 3, three motors</b>					
P0-ALL-AIM06-6	12.80	0.22	2.76	0.55	0.18
P1-ALL-AIM06-6	39.00	0.17	6.59	1.65	0.55
P2-ALL-AIM06-6	1.12	0.23	0.26	0.04	0.01
P3-ALL-AIM06-6	0.88	0.16	0.14	0.02	0.01
Average					0.12
Standard deviation					0.18
<b>Day 4, one motor</b>					
P0-ALL-AIM06-7	1.09	0.22	0.24	0.05	0.05
P1-ALL-AIM06-7	0.73	0.13	0.09	0.02	0.02
P2-ALL-AIM06-7	1.03	0.13	0.14	0.02	0.02
P3-ALL-AIM06-7	0.90	0.10	0.09	0.01	0.01
P0-ALL-AIM06-8	1.22	0.16	0.19	0.04	0.04
P1-ALL-AIM06-8	0.39	0.18	0.07	0.02	0.02
P2-ALL-AIM06-8	0.77	0.23	0.17	0.02	0.02
P3-ALL-AIM06-8	0.60	0.14	0.08	0.01	0.01

**Table 6-6 (cont'd). Witness plate results for 28 and 29 June.**

Sample	Perchlorate ( $\mu\text{g}/\text{L}$ )	Volume (L)	$\mu\text{g}/\text{row}$	$\mu\text{g}/\text{m}^2$	$\mu\text{g}/\text{m}^2$ per motor
<b>Day 4, two motors</b>					
P0-ALL-AIM06-9	matrix problems	0.18			
P1-ALL-AIM06-9	0.75	0.20	0.15	0.04	0.02
P2-ALL-AIM06-9	2.1	0.28	0.59	0.08	0.04
P3-ALL-AIM06-9	0.8	0.13	0.11	0.01	0.01
Average					0.02
Standard deviation					0.01
<b>Day 4, two motors: Results not available at time of report production</b>					
P5-ALL-AIM06-B1	nd	laboratory blank			
P5-ALL-AIM06-B2	nd	field blank			

### *Global Results*

The global results obtained from both media are presented in Table 6-7. In general, the quantities of perchlorate particles dispersed per square meter obtained with the use of witness plates are lower than those obtained with the use of water traps. This was expected, considering the higher risk of losing particles on the metallic surface because of the wind. Further calculations were based on the water trap results. An average global quantity of perchlorate dispersed by motor was calculated using water trap results. If we exclude samples W-17 to W-20 for Day 3, we obtain an average dispersion of 1.3 mg per motor. If we include W17 to W20 results, we obtain an average dispersion of 2.4 mg per motor. Considering the high uncertainty attached to these values, we can assume that 2 mg of perchlorate particles are dispersed by each motor. Mk58 motors contain 47 kg of AP; this means that we have measured a dispersion of only 2 mg out of 47,000,000 mg, resulting in  $4.25 \times 10^{-6}\%$  of perchlorate expelled per motor. This value is considered negligible, especially during the actual flight of the missiles, where 2 mg are dispersed over a distance of approximately 50 km.

<b>Table 6-7. Global results.</b>				
<b>Total quantity of AP dispersed per motor</b>				
<b>Day</b>	<b>Water trap result average conc. (<math>\mu\text{g}/\text{m}^2</math>)</b>	<b>Witness plate result average conc. (<math>\mu\text{g}/\text{m}^2</math>)</b>	<b>Surface area impacted (<math>\text{m}^2</math>)</b>	<b>Total AP dispersed (mg)</b>
1	0.5	nd	4000	2
2	0.4	0.2	4000	1.6
3	0.2	0.1	3000	0.6
3	7	0.1	1000	7
4	0.2	0.02	4000	0.8

## Conclusions

The present study is one of the first ever published on the assessment of the dispersion of perchlorate in the environment during normal burning conditions of tactical missile motors. Static firing was appropriate for this goal, since it keeps the residues in the smallest area possible. Even with static firing, we have seen that for medium-range rockets such as the Mk58 motors, a sampling template of  $4000 \text{ m}^2$  did not succeed in covering the overall dispersion of perchlorate. A larger sampling area that would have allowed the complete delineation of the AP particle plume would be needed to calculate a better estimate of AP dispersed. We underestimated the proportion of perchlorate emitted during the static firing of rockets motors. It would be interesting to repeat this experiment with a setup that would allow reaching the boundary area impacted with perchlorate particles.

Another conclusion of this study is that the percentage of solid AP dispersed by the static firing of Mk58 motors is very small and quite homogeneous over our sampling template. The low dispersion of perchlorate particles was expected since perchlorate is a very good oxidizer, which leads to propellants that are well oxygen-balanced with high burn rate. The combustion process is, therefore, very efficient and almost all perchlorate is transformed into hydrochloric acid. If we assume that the perchlorate dispersed is underestimated by a factor of 10, we would still have a negligible weight-to-weight percentage of perchlorate dispersed of  $4.25 \times 10^{-5}\%$ . The solid propellant of Mk58 motors is representative of the various formulations used in modern AP-based motors. Therefore, we may assume that the combustion efficiency of similar missiles should be very good, leading to a low dispersion of perchlorate particles. We have not included in the

present study other contaminants of concern, such as the anti-oxidant used in Mk58 propellant, phenyl-beta-naphthylamine. This latter compound is present at less than 1% by weight in the propellant but it might be considered as a health hazard since it has adverse toxicological impacts. Considering the low levels of perchlorate dispersed, we do not foresee that measurable quantities of this analyte could have been detected in any sample. However, it may burn less efficiently than the oxidizer and future trials might include it as an analyte.

The range of the Mk58 motor or the AIM-7 rocket is approximately 50 km. So, at the most, if we include a factor of 10 times over what we found, 20 mg of perchlorate would be dispersed in the environment over a 50-km-wide area at a high altitude. This means that the use of AIM-7 in live-fire training over our ranges does not contribute to any measurable impact in terms of perchlorate deposition/accumulation. This is also probably true for other AP-based rockets. This is not true for air-to-ground launches, when the rocket may reach the target before completely burning its propellant. In these circumstances, the remaining propellant might be either consumed in the detonation fireball upon impact, or else be dispersed in the environment if the detonation process is incomplete or inefficient.

Accumulation of perchlorate on test sites where static burning of AP-based rockets are conducted might happen, but considering the small impact per motor, the frequency of static firings would have to be quite high to reach levels of concern of perchlorate. Caution should be maintained for such sites, especially if frequent static firings of AP-based motors are conducted on a specific test site. An approximation of the concentrations of perchlorate could be estimated using this study, but sampling of the surrounding soils and groundwater should be conducted to confirm the results.

Another potential measurable source of perchlorate in the environment could be very large solid rocket motors, such as the booster used for the Space Shuttle. For example, approximately 70 percent of the weight of the solid propellant in the Space Shuttle boosters consists of ammonium perchlorate (Ref. 23). Each pair of Shuttle motors uses about 1.7 million pounds of ammonium perchlorate; thus, the Space Shuttle is the largest user of ammonium perchlorate and repeated use of the same site for vertical launches might present a risk for perchlorate accumulation.

The main conclusion of the present study is that the use of AP-based rocket motors in live-fire training by our troops does not represent a high potential source for perchlorate in the environment. Most of the propellant is consumed during the burning and the remaining small unburned portion is dispersed in the wide trajectory of the rocket.

## References

1. **Kohga, M.** (2006) Burning characteristics of AP/HTPB composite propellants prepared with fine porous or fine hollow ammonium perchlorate. *Propellants, Explosive and Pyrotechnics*, Vol. 31, No. 1, p. 50–55.
2. **Bennet, R.R., J.C. Hinshaw, and M.W. Barnes** (1992) The effect of chemical propulsion on the environment. *Acta Astronautica*, Vol. 26, No. 7, 531.
3. **Lessard, P., L. Druet, S. Villeneuve, S. Thiboutot, M. Benchabane, and D. Alexander** (1992) Development of a minimum smoke propellant based on glycidyl azide polymer and ammonium nitrate. NATO Advisory Group for Aerospace Research and Development, AGARD Conference Proceedings, AGARD-CP-511 on Insensitive Munitions.
4. **Stowe, R.A., P. Lessard, G. Roy, G. Richer, and M. Benchabane** (1995) Evaluation of ammonium nitrate propellant emissions, NATO Advisory Group for Aerospace Research and Development, AGARD Conference Proceedings, AGARD-CP-559 on Environmental Aspects of Rocket and Gun Propulsion.
5. **Jones, D.G, Q.S. Kwok, M. Vachon, C. Badeen, and W. Ridley** (2005) Characterization of ADN and ADN-based propellants. *Propellants, Explosives, Pyrotechnics*, Volume 30, Issue 2, p. 140–147.
6. **Weiser, V., N. Eisenreich, A. Baier, and W. EckBurning** (1999) Behaviour of ADN formulations. *Propellants, Explosives, Pyrotechnics*, Volume 24, Issue 3, p. 163–167.
7. [www.serdp.org](http://www.serdp.org) a) **Dewey, M.**: Synthesis, evaluation and formulation studies in new oxidizers as alternatives to ammonium perchlorate in DoD missile propulsion applications (<http://www.serdp.org/research/PP/PP-1403.pdf>).  
b) **Kendall, R.**: Ecological risk assessment of ammonium perchlorate in fish, amphibians, and small mammals (<http://www.serdp.org/research/upload/CU-1223.pdf>).
8. **Clewell, R.A., E.A. Merill, K.O. Yu, D.A. Mahle, T.R. Sterner, D.R. Mattie, P.J. Robinson, J.W. Fisher, and J.M. Gearart** (2003) Predicting fetal perchlorate dose and inhibition of iodide kinetics during gestation: A physiologically based pharmacokinetic analysis of perchlorate and iodide kinetics in the rat. *Toxicological Sciences*, Vol. 73, p. 235–255.
9. **US EPA** (2005) Drinking Water Contaminant Candidate List 2 (CCL) ([www.epa.gov/safewater/ccl/ccl2.html](http://www.epa.gov/safewater/ccl/ccl2.html)).

10. **Hatinzger, P.** (2005) Perchlorate biodegradation for water treatment. *Environmental Science and Technology*, Vol. 39, p. 239A–247A.
11. **Hatzinger, P.B., C.M. Whittier, M.D. Arkins, C.W. Bryan, and W.J. Guarini** (2002) In-situ and ex-situ bioremediation options for treating perchlorate in groundwater. *Bioremediation*, Vol. 12, p. 69–86.
12. **Hogue, C.** (2005) Federal policy on perchlorate evolves. *Chemical & Engineering News*, Vol. 83, No. 9, p. 35–36.
13. **Helm, B.** (2005) Perchlorate: Out of the hot water? *Business Week Journal*, p. 14–15.
14. **Bergman, C.** (2005) EPA Sets reference dose for perchlorate (<http://yosemite.epa.gov/opa/admpress.nsf/0/c1a57d2077c4bfda85256fac005b8b32>).
15. **Lang, V.I., K.R. Bohman, J.T. Tooley, E.W. Fournier, B.B. Brady, and M. Easton** (2003) Assessment of perchlorate releases in launch operations. Aerospace Report No. TR-2003 (1306)-2, prepared for Space and Missile Systems Center Air Force Space Command by the Aerospace Corporation.
16. **Dubé, P., S. Thiboutot, G. Ampleman, M. Bouchard, A. Marois, and A. Gagnon** (2006) Preliminary assessment of the dispersion of propellant residues from the static live firing of 105-mm rounds, DRDC-TM-2005-284.
17. **Walsh, M.R., M.E. Walsh, C.A. Ramsey, R.J. Rachow, J.E. Zufelt, C.M. Collins, A.B. Gelvin, N.M. Perron, and S.P. Saari** (2006) Energetic residues deposition from 60-mm and 81-mm mortars, ERDC-CRREL TR-06-10.
18. **Directory of U.S. Military Rockets and Missiles** (2002–2005) Aim/RIM-7 (<http://www.designation-systems.net/dusrm/m-7.html>).
19. **FAS Military Analysis Network** (2000) AIM-7 Sparrow (<http://www.fas.org/man/dod-101/sys/missile/aim-7.htm>).
20. **Lussier, L.S., F.C. Wong, and S. Villeneuve** (2002) Service life assessment of the ADATS rocket motor, DRDC Valcartier TR 2002-110.
21. **Wong, F.C., S. Villeneuve, and S. Côté** (2003) AIM-7 Sparrow Mk58 service life assessment—2001 test year, DRDC Valcartier TR 2003-005.
22. **Galligan C., R. Stowe, T. Gamache, and M.C. Lapointe** (in prep) ADATS motor smoke analysis from live static firing and laboratory tests, DRDC Valcartier TM.
23. Laws and Regulatory Policies (2003) Section 4: Perchlorate-containing products. [http://www.dtsc.ca.gov/LawsRegsPolicies/Regs/upload/HWMP\\_WS\\_dPerch-Sec4.pdf](http://www.dtsc.ca.gov/LawsRegsPolicies/Regs/upload/HWMP_WS_dPerch-Sec4.pdf)

**APPENDIX 6-A. SYMBOLS, ABBREVIATIONS, ACRONYMS,  
AND INITIALISMS**

ADATS	Air Defense Anti-Tank System
AP	Ammonium perchlorate
CTPB	Carboxy terminated polybutadiene
DGAEPM	Director General of Aerospace and Engineering Program Management
DND	Department of National Defence
DRDC	Defence R&D Canada
EPA	Environmental Protection Agency
ER	Environmental restoration
FPS	Frames per second
HTBP	Hydroxyl terminated polybutadiene
kN	kilo Newton
METC	Munitions Experimental Testing Center
PBNA	Phenyl-beta-naphthylamine
RDX	1,3,5-hexahydro-1,3,5-trinitrotriazine
SERDP	Strategic Environmental R&D Program

# REPORT DOCUMENTATION PAGE

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<b>14. ABSTRACT</b>  The objectives of the research described in this report are to characterize the deposition and accumulation of propellant residues at the various types of firing points at military firing ranges, develop process descriptors to allow estimation of environmental transport rates of individual energetic chemicals from these residues, and collect lysimeter and groundwater monitoring well samples to experimentally assess off-site transport of residues. Estimates of residue deposition are presented for the firing of 60- and 81-mm mortars and 105-mm howitzers. Experimental results are provided for propellant residue accumulation at antitank rocket, mortar, artillery, and small arms ranges at several installations. Results from soil column experiments on the transport of nitroglycerin, nitroguanidine, and diphenylamine also are presented with resulting transport property estimates. Also, an experiment to assess the deposition of ammonium perchlorate from Mk58 rocket motors is described.							
<b>15. SUBJECT TERMS</b>		Deposition Artillery Columns	Energetics Dinitrotoluene DNT	Nitroglycerin Nitroguanidine Perchlorate	Propellants Residues Rocket motor	Sampling Small arms Soil	Transport
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